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1954-1955

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THE Association was organized in Boston, Mass., on June 21, 1882, with the object of providing its members with means of social intercourse and for the exchange of knowledge pertaining to the construction and management of water works. From an original membership of only TWENTY-SEVEN, its growth has prospered until now it includes the names of over 900 men. Its membership is divided into six classes, viz.:

A Member shall be an officer or employee of a public or private water works, an engineer, chemist or other person qualified to aid or interested in the advancement of knowledge relative to water works.

An Honorary Member shall be a person of acknowledged eminence in some branch of water supply or of engineering.

A Junior shall be not less than eighteen years nor more than twenty-five years of age, a student or connected with water supply work.

An Associate shall be either a person, firm or corporation engaged in manufacturing or furnishing materials or supplies for the construction or maintenance of water works.

A Corporate Member shall be either a Water Board, Commission, Company or Municipal Corporation.

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This Association has at least eight regular meetings each year, of which five are held in Boston, one in northern New England, one in southern New England, and one, the annual convention, held in September or October on such date as the Executive Committee may designate.

ERRATA

The committee report, "Determination of Water Rate Schedules," was incorrectly bound in the December, 1954, issue.

Pages 9-24 are out of place and should appear between pages 8 and 25.

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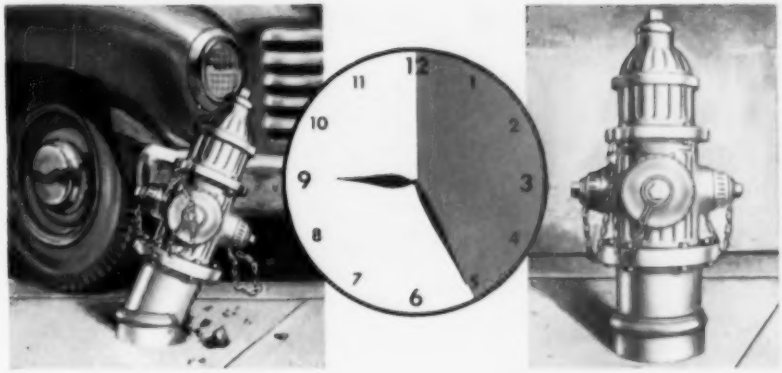

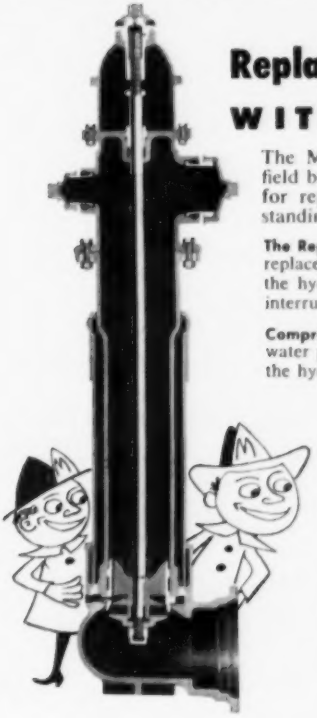

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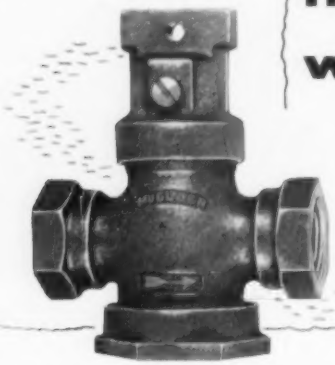

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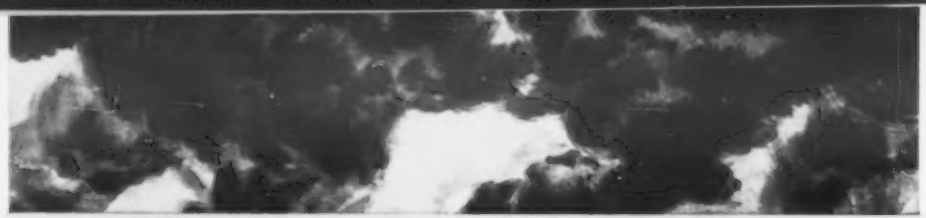

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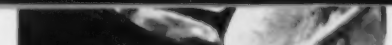

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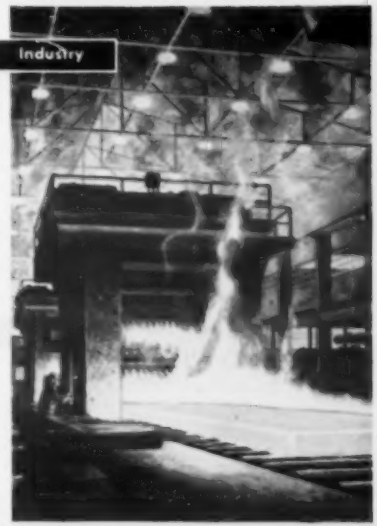

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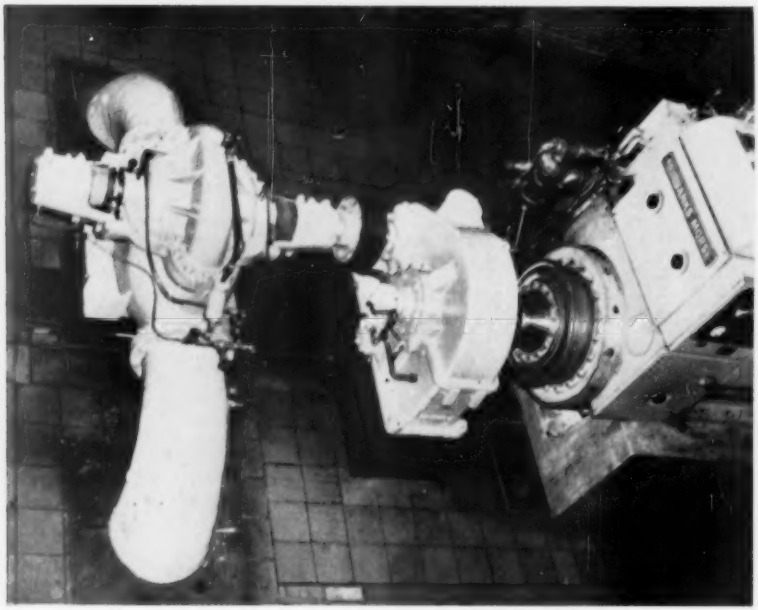

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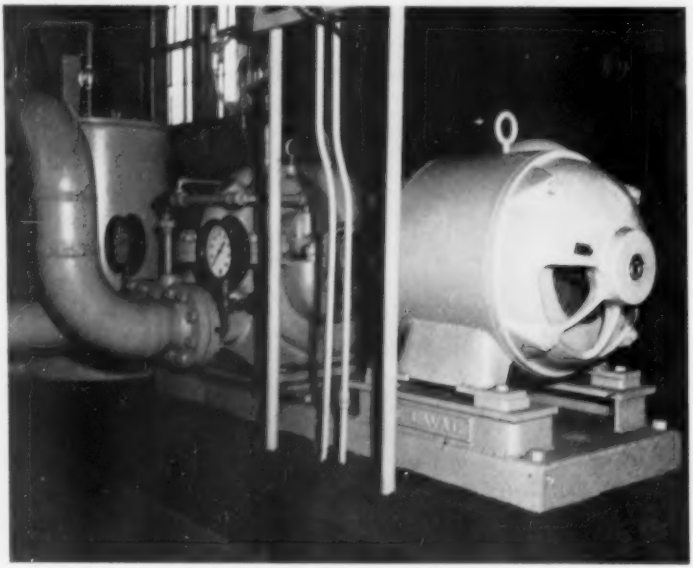

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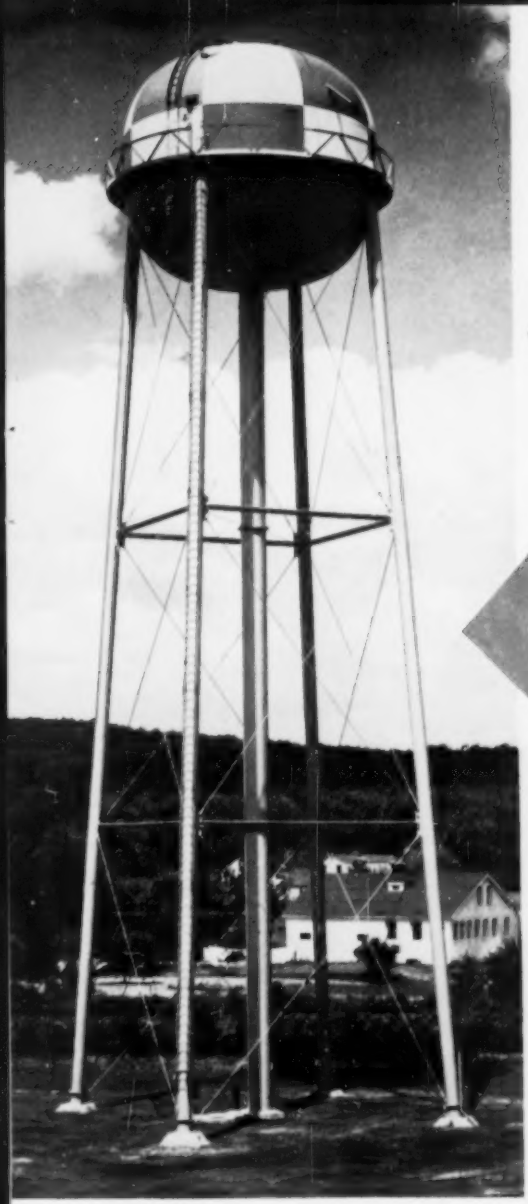

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Table of Contents

PAGE

Portrait of President Roger G. Oakman ..... Frontispiece

Status of the Membrane Filter in the Bacteriological Examination of Water
By John H. Bush 1

Non-Standard Methods of Analysis
By Ernest A. Snow, Jr. 9

Problems of Corrosion
By A. G. Smith 24

Corrosion Control with Metaphosphate Glass
By James C. Lamb, III, and Rolf Eliassen 31

How to Secure Maximum Benefits with Activated Carbon
By Albert Y. Hyndshaw 69

Chlorination—Theory versus Practice
By V. W. Langworthy 78

The West Boylston Water District Water System
By Louis C. Campbell 83

Determination of Charges for Public Fire Protection
By Darrell A. Root and Thomas R. Camp 90

Proceedings:
November 1954 Meeting 115
December 1954 Meeting 116
January 1955 Meeting 117

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ROGER G. OAKMAN
President of the New England Water Works Association
1954-1955

New England Water Works Association
ORGANIZED 1882

VOL. LXIX MARCH, 1955 NO. 1

This Association, as a body, is not responsible for the statements or opinions of any of its members

STATUS OF THE MEMBRANE FILTER IN THE BACTERIOLOGICAL EXAMINATION OF WATER

BY JOHN H. BUSH*

[*Read at Chemists' Round Table, Nov. 19, 1953.*]

The membrane filter was developed in this country originally under the sponsorship of the Army Chemical Corps for its application in rapid detection methods for biological warfare agents. The Lovell Chemical Co. assumed the charge of reducing a laboratory bench process of making the filter to mass-production methods, to fill the needs of the military. Incidental to this work has been the establishment of the most rigid controls of processes of production. It is the unique structure of the MF and the degree of uniformity that has defined its usefulness. The end product was declassified in 1951 in the interest of making this new tool available in the field of public health. Since that time a great deal of research has been devoted to the development and refinement of bacteriological techniques, with special reference to water-analysis procedures.

The membrane, which we have called the Millipore Filter, resembles paper in appearance, but there the similarity ends. It is perhaps useful to think of the membrane structure as similar to a section of a honeycomb, the hexagonal openings of which are reduced to submicroscopic size. It may also be likened to a sieve, or two-dimensional screen, presenting an absolute barrier to particles in a liquid 0.45 micron in diameter or greater. Performance confirms the validity of these analogies. Approximately 80% of the volume of the MF sheet is occupied by uniform pores which are perpendicular to the plane of the surface. Thus, the number of pores defined by this structure is calculated to be 50 million per square centimeter.

The significance of this new device in bacteriology is, however, only partially described in terms of quantitative surface screening of

*Millipore Filter Corp., 36 Pleasant St., Watertown, Mass.

bacteria. Bacterial cells retained from a dispersion on the two-dimensional surface find themselves in a novel and unique environment. Like flagpole sitters depending on supplies from a bucket on a rope, they are perched on pinnacles defined by the millions of capillaries perpendicular to the plane of the filter surface. Nutrient is supplied to these isolated cells, independently, by the capillaries, and utilized more or less according to nutritional requirements. The simple bacteriological procedure involves the transfer of the MF disc after filtration to an absorbent pad, saturated with liquid nutrient, and subsequent incubation. Rapid growth characteristics of a wide range of microorganisms on the filter surface permit more rapid methods of identification. Culturing conditions are subject to control not obtainable with other microbiological procedures. There is no interaction or antibiotic action between bacterial colonies on the MF surface when reasonable concentrations are cultured on the surface, as is the case with colonies cultured in broth tubes and to a somewhat smaller degree on agar plates. Sample size may be many times the amount used in other bacteriological procedures, which also contributes to the accuracy and sensitivity of MF methods.

Figure 1 shows the simple glass filter apparatus which may be used in the estimation of coliform organisms in water supplies with the MF. The membrane is supported by a coarse fritted glass disc and sealed on the edges with clamping flanges. A stainless steel filter unit is also available, which offers versatility in bacteriological procedures. Organisms suspended in the water sample are reduced to the MF surface as the water passes through the membrane. After filtration, the MF is transferred to an enrichment medium, which has been introduced into an absorbent pad, incubated for a two-hour period, and subsequently transferred to a differential medium, such as the LCC "modified Endo medium" described by Yee, Krabek and Schaufus (1). After a 16- to 18-hour incubation on the LCC medium, the coliform organisms are distinguishable by the formation of a metallic sheen. Figure 2 shows a culture of bacteria from a water sample and indicates the inhibition of non-coliform "background" organisms, to permit the proper development of the coliform organisms. Reference is made to the attached bibliography for further details of MF procedures, as applied to water bacteriology.

FIG. 1.—GLASS FILTER APPARATUS USED WITH MEMBRANE FILTER.

A method using the membrane filter in the enumeration of coliform organisms in water has been accepted by the Coördinating Committee of Laboratory Methods and the Executive Committee of the American Public Health Association, as recommended by the Subcommittee of Standard Methods for the Examination of Water and Sewage, for publication as a tentative procedure to appear in the tenth edition of Standard Methods for the Examination of Water and Sewage. The adoption of this procedure has been based on the results obtained from a coöperative field study under the joint auspices of the American Public Health Association, the American Water Works Association, and the Environmental Health Center of the United States Public Health Service. These results were reported by Dr. Paul Kabler, Chief, Bacteriology Section of the Environmental Health Center at the annual meeting of the American Public Health Association in November, 1953, in New York. Eight participating laboratories have provided the test data of the coöperative study.

An independent study conducted at our laboratory, comparing the MPN (Most Probable Number) method with the MF method employing the LCC (modified Endo medium), has been reported (1). Samples were chosen from various water sources: reservoirs, wells, finished waters, and rivers. Ten MPN analyses were prepared for each water source, five tubes being used for each dilution, and three or more dilutions for each sample. Positive tubes were confirmed on EMB agar after 24 and 48 hours. Results were compared with ten MF determinations on each water source, as is described in detail in this paper. Results may be summarized as follows:

1. Application of the MF membrane with the LCC medium to the examination of surface, ground and finished waters showed good correlation with results obtained using the MPN procedure.

2. The membrane filter method using the LCC medium showed the presence of coliform organisms in many tests in which the MPN failed to do so.

3. With the membrane-filter method, approximately 81% of the sheen colonies and approximately 22% of the nonsheen colonies produced gas in lactose upon subculturing.

4. The membrane-filter method permits the testing of larger and more representative samples of water than the MPN method.

FIG. 2.—CULTURE OF BACTERIA FROM A WATER SAMPLE, ON ENDO-TYPE MEDIUM

A preliminary statistical analysis of the data resulting from these comparative tests may be summarized as follows:

1. The means of the coliform counts derived from the MF and MPN determinations are related.

2. Variability and standard deviation of the MF is one-half as much as the MPN.

3. Standard deviation of the coliform counts is consistent for the MF and MPN.

4. One MF is equivalent as an index of population to four 5-tube MPNs.

This preliminary study of the data has been made with the kind assistance and guidance of Dr. Muench of the Biostatistics Department of the Harvard School of Public Health.

From the preceding one may say in summary that comprehensive testing in the field with a wide variety of water samples has established that the MF procedures for the determination of coliform organisms in water yield a more sensitive and reliable index than the MPN method.

Results are available in a very much shorter time (18 hours as against 72 to 96 hours for the MPN procedure).

A study of economic factors incidental to the extensive comparison of the two procedures at this laboratory has revealed that there are very substantial savings in overall costs of the MF procedures as compared with the MPN, and a very significant reduction in operational time. This will permit an extension and concentration of sanitary control of water supplies.

The foregoing would appear to be valid reasons for establishing the MF in water-bacteriology laboratories. There is, however, another extremely compelling reason. At the several meetings of the American Public Health Association convention in New York (November, 1953), concerned with civil defense, and more specifically contemplating the use of biological warfare agents, the common conclusion was that adequate monitoring and defense measures should be established with the state and local health authorities. Great emphasis was placed on methods of early detection of abnormal populations of micro-organisms and their early identification. Our water systems offer an established and highly efficient distribution system for BW

organisms, and a more foolproof means of dissemination than aerosols, which must depend on conditions of weather and wind. The communists have repeatedly accused us of using germ warfare. This cannot be without significance, and it could be logically assumed that this may be done to prepare subject people for the acceptance of their own usage of this insidious weapon. It is further suggested that although the Communist mind is not well understood in this country, a weapon that cripples and yet leaves production facilities intact would have an obvious appeal to an enemy lacking scruples and bent on world domination.

The water laboratories represent our first and, in all probability, our only line of defense against disease-producing organisms introduced by an enemy. If we discount the actual introduction of pathogenic organisms by an enemy, the devastation of saturation bombing inevitably threatens the uncontrolled spread of disease. Again, the common carrier would be our water systems and supplies.

Coliform population, which is an index of sanitary significance, would, of course, probably be of questionable value as an index of organisms introduced by an enemy. Total populations may be estimated rapidly and accurately by culturing on a medium which supports the growth of a wide range of organisms. Media have been developed and applied to the identification of specific pathogens with the MF where the filter again provides more sensitive and rapid procedures.

Dr. Victor Haas, head of the Government's Microbiological Institute has warned that (a) biological warfare is a definite possibility and (b) the U. S. is ill-equipped at present to ward off such an attack (10). The nation has too few facilities even for detecting the minute organisms that an enemy might use and no organization to combat the widespread disease they might cause.

What the U. S. needs, according to Dr. Haas, is a nationwide system of germ-warfare detection centers . . . a device to force large samples of air through filters on which disease-causing organisms would be trapped. Each day's catch could be analyzed, to see whether any unusual microbes had appeared. So would samples of the area's milk and water supplies.

The adoption of MF procedures permits the intimate monitor-

ing of water supplies and the rapid initiation of corrective measures where indicated. Therefore, people who are giving thoughtful consideration to the protection of our public feel that either in the peacetime surveillance of the sanitary conditions of our water supplies, or in the wartime detection of bacterial agents, the MF represents a vital contribution.

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NON-STANDARD METHODS OF ANALYSIS

BY ERNEST A. SNOW, JR.*

[*Read at Chemists' Round Table, Dec. 17, 1951.*]

Most sanitary chemists today probably would agree that there is too long a lag between the development of a new method of analysis and its adoption as a standard method. Perhaps the most glaring example is that of the dithizone method for lead, which is almost universally used but is still in the non-standard category (1).

It was in the interest of provoking discussion on this subject that the author agreed to give this paper at the Chemists' Round Table. In the writer's opinion, the most important criteria of acceptance of new methods should be the following:

1. Accuracy of the method
2. Speed of obtaining results
3. Stability of reagents
4. Simplicity of the test procedure

No doubt accuracy is of great importance, and for the benefit of the engineers our motto might well be, "Push those figures to the right of the decimal point." Although, from the nature of water samples, extreme accuracy is generally of little value, due to the longer time required to obtain it, yet, the more accurate the method, usually the more reliable the results (2).

In this age of jet planes and radar, speed is becoming a fad, if not an obsession. However, it is well to remind ourselves occasionally that there is no inherent value in speed. Be that as it may, there are some occasions when speed is required. For example, at times of floods and other emergencies, when work is being done under contract, and when changes are being made in water treatment, speed is necessary, if not even vital.

Since the introduction of so many organic reagents in water analysis, the question of stability of reagents has become important.

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In general, it may be said that many reactive organic compounds are unstable when kept at the normal laboratory temperatures or at summer temperatures, or when left in the sunlight. As an example, the well-known Griess reaction for nitrites, as employed in the Standard Methods procedure, calls for alphanaphthylamine reagent, which is notoriously unstable in heat and light and has to be made up quite frequently. In a newer modification of this method, the reagent is prepared with dimethyl alphanaphthylamine, which is much more stable and, if kept in the icebox, can be used for at least six months with just a slight darkening of the solution (3).

Since many of the tests in water analysis are conducted by analysts with little technical training, the simpler the test procedure the better. Complex operations usually require more time and more apparatus and, therefore, are more expensive than a simpler procedure which accomplishes the same results.

In addition to these four criteria, it would be well when developing new methods if more studies were made on the sources of errors in the tests. If the chief sources of error in a method are known, oftentimes one is able to prevent errors from creeping in. A few examples of sources of error in one of the newer methods using an organic reagent are the following in the determination of zinc by the dithizone method: Contamination of the reagent by metals, even though they are sold as chemically pure; contamination of distilled water and reagents on standing in various containers; interfering metals; leaving the reagent in direct sunlight; and the use of apparatus that is not chemically clean.

Listed below is a suggested outline for writing up new methods:

1. Purpose of the test
2. Sampling
3. Equipment needed
4. Reagents needed
5. Procedure
6. Results
7. Interpretation
8. Sources of error
9. References

Relatively New Non-Standard Methods

In the discussion following, I shall mention several methods of analysis that have been developed chiefly in the last twenty years and follow the order that is used in Standard Methods of Water Analysis. The first subject is that of *odors*. In the Standard Methods procedure, the method still used is the old and rather unenlightening method of reporting odor types by such terms as fishy, geranium, sweet, and grassy. To a perfume chemist, these terms would be meaningless, since they might cover a general group of several hundred organic compounds, each of which has a distinct odor of its own. Crocker and Henderson (4) of the A. D. Little Laboratories about 1927 developed a method of typing odors which uses a set of standards comprised of pure organic compounds. This method reports odors by a four-digit number system running from zero to eight for intensity, the first figure standing for the fragrant component, the second for acid component, the third for burnt and the fourth for caprylic. This method is described in a book by Crocker (5), called "Flavor," which is recommended to anyone interested in the subject. It seems to me that this system of typing odors could be adapted to water analysis, especially since more refined methods of separating odor constituents have been developed, using activated carbon as a collector (6). The reader is referred to the research on industrial waste odors being conducted at the U.S.P.H.S. station in Cincinnati, Ohio.

A method of determining *total solids* by electrical resistance is discussed in Standard Methods. It consists of finding the specific conductance of the sample as measured in reciprocal ohms x 10^{-5} at 25°C. and reading the total dissolved solids from a curve. This method can also be very useful for samples with very high total solids— e.g., above 1,000 ppm (7). Along this same line, Knowlton recently gave a paper on using this method for determining fluorides (8).

In the determination of *alkalinity*, the methyl orange endpoint has given a great deal of trouble both to students and persons with a slight case of color blindness. In recent years, several new indicators have been developed. The one using methyl orange and xylenecyanole seems to be quite satisfactory, although the endpoint is slightly lower than methyl orange alone. Bicarbonates can also be deter-

mined by using methyl purple, and several other indicators have been tried out (9) (10).

Although Standard Methods contains a method for *lead* (under the non-standard methods), using dithizone, the writer prefers to use a variation of this method which obviates the use of blanks. Instead of using dithizone solutions made up ahead of time, I make the reagent at the same time as the determination is made and extract the reagent, after the buffer has been added, with as many portions of carbon tetrachloride as needed to get rid of colors due to contamination.

Zinc can also be determined by dithizone, by means of the modification developed by Holland and Ritchie (11). In this method the writer also modifies it by extracting all reagents until free from chemical contamination, so that blanks are not required.

Both lead and zinc determinations can best be carried out with a photoelectric colorimeter, using the proper filters, although visual methods are also usable.

Dithizone Method for Zinc in Detail

Preparation of reagents:

1. Double-distilled water.

   Single distilled water from a Barnstead still is redistilled in a Kjeldahl flask (500 or 1,000 ml), using a few drops of sulfuric acid in the water. Collect in glass flask and store in pyrex 1 L. bottles with ground glass stoppers.

2. Standard zinc solution.

   Stock solution: 1 cc = 0.001 gm; (2 gm pure zinc foil in 2 L.) Dilute solutions: take 1 cc stock solution, dilute to 200 cc; then 1 cc = 0.005 mg.

3. Ammonium hydroxide.

   Add 11.2 cc conc. NH_4OH to 1 L. double-distilled water = 0.2 N.

4. Sodium diethyl dithiocarbamate.

   2.5 gm per 1 L. double-distilled water. Keep cool in *amber* bottle. Make up fresh every week or so. Use 0.25 g/L. if preferred.

5. Diphenylthiocarbazone or dithizone.

   Dissolve a pinch (about 0.02 gram) of dithizone (E.K.) in 10 cc of the NH_4OH (reagent #3) in a separatory funnel (250 cc), add

55 cc of water and 10 cc CCl_4 (see below) and let stand 5 minutes. Shake 30 times and let stand 5 minutes. Draw off the CCl_4 and save it for recovery. Shake out with another 10 cc CCl_4. Filter the yellow aqueous solution through a washed filter paper into an *amber* bottle. Prepare this solution daily, or as often as needed. It will only keep a few *hours*.

6. Ammonium citrate solution.

Dissolve 112 gm in 800 ml double-distilled water, add conc. NH_4OH until sharply alkaline to litmus, and make to 1 L. with double-distilled water. Whenever needed, put 250 cc of this citrate in a separatory funnel, add a little solid dithizone and shake out with 10-25 cc portions of CCl_4 until color goes from pink at first to yellow-green. If a blue-green color remains, it contains zinc. Preserve in a 500-cc pyrex bottle (ground glass stopper).

7. Carbon tetrachloride.

Redistill all CCl_4 used, even that marked C.P., since it gives a test for zinc with dithizone. The CCl_4 can be redistilled after separating it from water layers in a funnel, as is, or over anhydrous sodium sulfate. Either way seems satisfactory. *Never* distill all the CCl_4, but have about ½ inch of liquid in the flask, cool and stopper before leaving until the next batch is redistilled. All the residues from the zinc tests are saved and redistilled. Even though the distilled CCl_4 is cloudy from water, it does not affect the determination, since it is used right over again in water.

Procedure:

If the approximate amount of zinc in the sample is known, use an amount to give a color between 1 and 5 ml of the dilute zinc solution #2.

E.g., use 1 cc if Zn is 5-15 ppm
2 cc if Zn is 3-10 ppm
2.5 cc if Zn is 2-5 ppm
5 cc if Zn is 1-2 ppm
10 cc if Zn is 0.1-0.2 ppm
50 cc if Zn is 0.1 ppm

Ex.: Take 5 cc of sample, add it to the extraction mixture which is made as follows: Into the separatory funnel (250 cc), pipette or measure in graduate 5 cc carbamate, 5 cc 0.2N NH_4OH, 10 cc citrate

reagent, 1 cc of dithizone solution, and make up to 55 cc with double-distilled water.

Shake 30-35 times with CCl_4 (redist.). Pour the CCl_4 layer and any water in excess of 50 cc into a Nessler tube (50 cc). Add 1 cc of dithizone and 10 cc CCl_4, and repeat. Generally the colors are #1 = pink, #2 = purple, #9 = green; or, if the reagents are very pure, #1 blank = purple to blue-green, #2 = yellow-green. Save these as comparators. Now make stds. with 0.5, 1, 2, 3, 4, and 5 cc of dilute zinc standard.

After standards have been made up and marked in Nessler tubes, shake the sample (5 cc) with 1 cc dithizone and 10 cc CCl_4. Compare the color in the tubes against a white porcelain plate in a good light, but not in direct sunlight. Sunlight destroys the dithizone reagent and the metal complexes in very short order. It also affects the dithiocarbamate. The latter is used to prevent interference from copper, which gives a yellow color in alkaline dithizone. However, the copper must not be present in amounts over 5 ppm. When copper is present in excess, the sample must either be diluted enough to lower the copper or else be removed by precipitation. E.g., when a sample contained 1.7 ppm copper, only 2 cc was used to determine the zinc; otherwise, off colors, such as a chocolate color, were obtained with dithizone. The colors of the tubes are about as follows:

First blank = purple to blue-green
Second blank = blue-green to yellow-green
(pure) Dithizone = yellow-green
0.05 = purple
0.10 = pink
0.20 = pink with trace of yellow
0.30 = pink with more of yellow
0.40 = salmon
0.50 = salmon (more yellow)
above 0.5 = increase in yellow shade, but difficult to distinguish by eye

The advantages of using the same extraction mixture over and over are twofold. First, it saves time and reagents, instead of making the mixture for each sample. Second, it eliminates running blanks and making corrections on each sample, since we start each time with

a zero blank and, if necessary, the blank can be made before each extraction (if previous sample was very high), but this is seldom necessary.

One difficulty occasionally encountered is that the dithizone is too dark, or too much is used, and the samples have too much green in them; this trouble can easily be avoided by using less dithizone reagent. If the dithizone stands over an hour, larger amounts must be used to get equivalent strengths.

Summary:

The dithizone method for zinc, by Holland and Ritchie, has been adapted for the analysis of small amounts of zinc in water. The method is colorimetric and very rapid and accurate, as compared to the older methods. More skill is necessary, however, to get reproducible results.

In both the lead and zinc determinations, copper will interfere if present in amounts over 2.0 ppm (approximately). In one case of a lead-poisoning investigation which we encountered, it was necessary to determine if any lead was present in tea when made in a pewter pot. In this case, it was necessary to separate the copper from the tea before extracting the lead. This was done by adding salicylaldoxime and 30% acetic acid. The copper precipitated out and was filtered, and the lead was determined on the filtrate.

As late as 1950, *calcium* was determined by subtracting the magnesium result from the total hardness. It is now possible to determine calcium directly by titration with versenate, using ammonium purpurate as the indicator in a strongly alkaline solution (12).

The determination of *sodium* and *potassium* has been a difficult procedure and the results unsatisfactory, until the new flame-photometer method was developed. Although this method requires expensive apparatus, hundreds of determinations can be made in a relatively short time, with greater accuracy than can be obtained with the older quantitative methods (13).

In the determination of nitrates, the preparation of the phenoldisulfonic acid has often given trouble. A new method, using salicylic acid in place of the phenoldisulfonic, was reported in Public Health Engineering Abstracts, July, 1943 (14). This method consists of converting salicylic acid to picric acid in sulphuric acid solution by

nitration, and colorimetric comparison of the sodium picrate formed with standards. It was developed by Jokhel'son in the U.S.S.R. in 1941.

Purpose of the test:

To determine the total oxidized nitrogen of a sample and to show the relative amount of nitrates compared to the ammonia and nitrite nitrogen. This newer method supersedes the older phenol-disulphonic acid method with obvious advantages.

$$3HNO_3 + C_6H_4(OH)COOH \rightarrow C_6H_4(NO_2)_3OH + 3H_2O + CO_2$$

Sampling:

The sample should be collected fresh and the nitrate determined as soon as possible, as the amount generally increases on standing, unless it is utilized by growing algae.

Equipment:

Small evaporating dishes
Electric or other heater or water bath
Pipette 20 ml (vol. type)

Reagents needed:

10% salicylic acid in 95% alcohol
Concentrated sulfuric acid
Clear sodium hydroxide (15% to conc'd)

Procedure:

Evaporate 20 ml of sample to dryness on hot plate. Do not overheat when dry, but remove dish at once. Let cool, add several drops of salicylic reagent and 1 ml conc. H_2SO_4, stir and rub in with glass rod, so that all the residue comes in contact with the liquid. Let stand 10 minutes. Add 5-10 ml distilled water and stir. Add slight excess of strong NaOH; yellow color shows nitrate. Check by streaking hydrion paper with the stirring rod. Blue color proves sample is alkaline. Compare sample in Nessler tubes with standards or in colorimeter. Decant liquid from evaporating dish, wash with distilled water until Nessler is up to mark. Mix by inverting tube, using boiled rubber stopper. *N.B.* If photoelectric colorimeter is used, all volumes should be the same on the blank and the sample.

Results:

Express to 2 significant figures in ppm or as follows: 0.03 (never .003), 1.6 (not 1.62), 32. (not 32.1), etc.

Interpretation:

Nitrates in water are commonly reported in terms of nitrogen. In mineral analyses nitrates are usually reported in terms of the radical NO_3. Since nitrates are products of oxidation of ammonia and nitrites, samples should be run when fresh. Surface waters are generally low in nitrates. Well waters may be high in nitrates from animal feces and urine, as well as from sewage and highly fertilized soils.

High nitrates not only point to possible pollution, but are harmful in themselves to infants. Methemoglobinemia is caused by nitrates when over 20 ppm. "Blue babies" is the term commonly used by laymen to describe this often fatal condition in infants. *N.B.* Other nitrogen compounds may be involved.

Sources of error:

Overheating residue in porcelain dish
Inadequate rubbing-in of acid and reagent
Precipitate formation in very hard waters
Natural color or high values
Excess iron or other colored substances with the reagent
Nitrite, chloride and carbonate do not interfere

References:

Jour. Amer. Water Works Ass'n, 34:1460, Sept., 1942
Amer. Jour. of Public Health, Vol. 40, No. 7, 866-7, July, 1950

Calculations:

Milliliter of standard nitrate x 50 = the parts per million of nitrate nitrogen.

If any amount of sample is used other than 20 ml, divide 1,000 by the ml used and multiply by the reading on the standards.

It is obvious that the salicylic reagent is very easily made up and does not spoil with age.

I have already mentioned the use of dimethyl alpha-napththyl-

amine in the determination of *nitrites*. This reagent is advocated by the A.O.A.C. and is described by Jacobs (15) in "Poisons, Hazards, and Solvents."

Chlorides may be determined, even when present in large amounts by titration with mercuric nitrate, using diphenylcarbazone bromophenol blue mixed indicator (16).

In view of the interest in fluoridation of water, it might be of interest to mention a modification of the alizaran zirconium method for the determination of *fluorides*. The Megregian and Maier modification of the zirconium alizarin method was adapted for use with a simple filter photoelectric colorimeter (17). The reagent is prepared from sulfuric acid only, instead of a mixture of sulfuric and hydrochloric. The reasoning behind this is that the reaction is complex enough at best, so why add hydrochloric acid? The method is to set up a series of standards, including a zero blank, together with the samples, in 100-ml tall-type Nessler tubes. Add 5 ml of reagent, let stand one hour, and then read on the photoelectric colorimeter, using filter #520. A comparison of this method with others has been made and accuracy between 0.02 and 0.05 ppm can be obtained, if directions are followed and allowances made for interfering chemicals. It has been noticed that, by prolonging the time of contact, the results can be extended up to 3 ppm; by the one-hour method, the accuracy drops off just beyond 1 ppm.

Short Qualitative Methods for Boiler Sludge and Pipe Deposits

Kenneth Knowlton of the Salem-Beverly Water Department suggested that the author include some short qualitative tests for substances likely to be found in boiler sludge and deposits on distribution pipes. There are three methods of testing which are commonly used outside of the standard procedures for qualitative tests and quantitative determinations. These are the so-called spot tests, semi-micro tests, and the use of the chemical microscope.

Spot tests are generally performed either on a white porcelain spot plate or on small squares of filter paper that have been impregnated with a water-repellent ring, to confine the drop of materials used and the reagents. Among the numerous spot tests, I shall give

five examples. An excellent test for *copper* is to put a drop of rubeanic acid, dissolved in alcohol, on the spot paper and allow it to dry. Apply a drop of the sample which has been put in solution with dilute nitric acid and filtered. Then expose the paper to strong ammonia fumes. A dark greenish-black precipitate shows the presence of copper.

The test for *zinc* is best performed on a spot plate and, although it is less sensitive than the dithizone test given above, it is usually sensitive enough for the amounts which would be found in boilers and pipes. Place a drop of Orange IV reagent with a drop of dilute sulfuric acid in the depression of the plate and add a drop of freshly prepared 2% potassium ferricyanide. The latter gives a red color which turns to green in the presence of zinc. Another variation is to use diethylaniline in place of Orange IV, which gives a red color. In using spot tests, if two different reagents give the proper color with a metal ion, it is considered absolute proof of the presence of the material for which one is testing.

For *aluminum*, the test can be conducted either on a spot plate or in test tubes. Aluminon gives a red precipitate with aluminum, which is insoluble in a mixture of ammonia and ammonium carbonate. Hematoxylin gives a purple flocculent precipitate in ammonia. It is well to run blanks with these tests, since hematoxylin is dark blue with alkalies.

In testing for *magnesium*, add excess oxine (in acetic acid) to a very dilute solution of the unknown. Add a trace of hydrochloric acid and warm. Add excess ammonia and let stand. The precipitate of fine long needles indicates magnesium. For the second test, titan yellow gives a bright red color with magnesium salts in excess sodium hydroxide, but the ordinary sodium hydroxide reagent contains magnesium, so it should be purified, adding the dye to it and then filtering through a fritted glass crucible.

The spot test for *iron* is to add a drop of sulfosalicylic acid to a drop of the sample. This gives a violet color with ferric iron. An even more sensitive test is to add one drop of aa'Dipyridyl reagent. A pink color indicates ferrous iron. A third test that can be used is to add a drop of oxine to the sample, which gives a dark green color or precipitate with ferric iron.

Some of the spot tests can be made quantitative when conducted on the spot-test paper and compared against standards made with standard solutions of the metals.

The methods of chemical microscopy are valuable in qualitative analysis for several reasons. By chemical microscopy we mean the use of a special microscope, with polarizing adjuncts, a revolving circular stage, which allows tests for physical properties, crystal form, etc., as well as the usual chemical reactions, producing special, easily recognized crystalline forms for identification of both cations and anions.

One example will suffice to show the ease of identification of a metal. Zinc ions, with potassium mercuric thiocyanate, give a characteristic crystal form in the shape of white feathery crosses. Mixtures of other metals with zinc give a variety of forms which can be used as a clue to the other ions present.

A very great advantage of this technique is the ability to identify actual molecular compounds present. An example of this is the following: trisodium *phosphate* with 10 molecules of water of crystallization is the only simple sodium phosphate which is isotropic. Therefore one small crystal, separated from a powdered mixture, if isotropic and positive for sodium and phosphate, would show that a triphosphate ($Na_3PO_4 \cdot 10\ H_2O$) is present. An actual example of this was noted when a paint-brush cleaning compound was analyzed; otherwise, the mixture was very complex and contained fillers, etc. This type of sample is often met with in the deposits in pipes and boiler sludge (ref. Chamot and Mason. Handbook of Chemical Microscopy. Wiley).

Semi-Micro Test-Tube Tests

The first example of this technique is the detection of traces of *hydrogen sulphide* in water according to the method in the Manual of Spot Tests by Feigl. Palatable drinking water must contain no hydrogen sulphide. As little as 0.5 ppm of sodium sulphide can be detected by a catalytic reaction between sodium azide and iodine. The reagent is prepared by dissolving 1 gram of sodium azide and 1 gram of potassium iodide in 3 ml of water. A small crystal of iodine is added. No reaction occurs even after months of standing

unless a catalyst is added. All forms of sulphur in sulphidic linkage give this reaction. The reaction is as follows:

$$2NaN_3 + I_2 \text{ or } \xrightarrow[(Na_2S)]{S=} 2NaI + 3N_2\uparrow$$

In testing for hydrogen sulphide, the sample (which should be collected fresh in the field and the test conducted at once) is placed in a tiny test tube and several drops of the reagent added to it. Many bubbles of nitrogen gas will appear at once if hydrogen sulphide is present. This test was first carried out by the writer while investigating a mineral spring which has been buried for approximately 100 years under soil and debris. The reaction was very sharp and definite, even in samples that had no obvious odor of hydrogen sulphide, and confirmed the analysis of this spring water made some time in the 1870's.

Another variation of this test is to extract the hydrogen sulphide by shaking the sample with a drop of mercury. The water is poured off and the mercury transferred to a watch glass. A few drops of the reagent are added and, if free sulphur or hydrogen sulphide is present, bubbles of nitrogen will stick to the mercury and are easily seen.

An extremely sensitive test for *manganese* is best carried out in the same type of small test tube as is used in the sulphide test. I quote directly from Snell and Biffen's book, "Commercial Methods of Analysis", page 97:

"In this test, manganese is converted to permanganate by periodate, which then serves to oxidize the reagent. In a sense the manganese acts catalytically since it will be oxidized to permanganate so long as excess periodate is present. Chromium salts will also be oxidized to chromates by the periodate, and this also oxidizes the reagent; therefore, chromium must be absent.

"To a drop of the solution under test, add a drop of a saturated solution of potassium periodate, a drop of 10 per cent acetic acid, and 2 drops of a 1 per cent solution of the reagent in chloroform. An intense blue color indicates the presence of manganese.

"The limit of sensitivity is 0.000001 mg of manganese in a concentration of 0.02 ppm."

The reagent is tetramethyldiaminodiphenylmethane. This test also was carried out on a sample of the spring water mentioned previously and was positive.

Summary

It has been pointed out that there are at least four criteria of acceptance for standard methods of water analysis and that the order of their importance is probably as follows:

1. The accuracy of the method
2. Speed of obtaining results
3. Stability of reagent
4. Simplicity of the test procedure

Examples of several non-standard methods have been chosen to illustrate several different techniques, such as the use of spot-test methods, semi-micro methods, and chemical microscopy. Most of these new methods are modifications of old tests with modern improvement, but a few are new tests making use of some of the newer organic reagents. Whereas some of the methods are quantitative and extremely sensitive, others are only good for qualitative tests; *e.g.*, to give an indication of what metals are present in a pipe deposit.

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PROBLEMS OF CORROSION

BY A. G. SMITH*

[*Read at Chemists' Round Table, Jan. 21, 1954.*]

Many people consider problems of corrosion in fresh water systems to be rather simple compared with those encountered in, say, a chemical plant. It is true that in chemical operations we have severe problems in finding materials of construction which will satisfactorily survive exposure to intensive corrosion media, such as strong acids, alkalis, halogens or oxidizing agents. These problems, however, are usually fairly specific and when they are solved by the use of expensive materials of construction, the involved cost becomes part of the price of the product.

In fresh water applications, however, corrosion is a problem both vexing and subtle, as it is usually the combined result of many small but appreciable influences, and the engineer is required to correct the problem without spending any appreciable money.

Corrosion may be defined as the destruction of materials of construction by chemical or electrochemical action. When it is assisted by mechanical disturbances, the resultant destruction is known as conjoint action, examples of this being corrosion fatigue and cavitation.

Corrosion occurs in three principal mechanisms in aqueous media:

1. Direct attack of the corrosion agent on a metal.
2. Two-stage attack, wherein products of corrosion which tend to slow the action are disposed of by additional reactions occurring some distance from the metal, thereby allowing the primary corrosion reaction to continue.
3. Electrochemical attack, wherein the products of corrosion are removed by an electrical circuit within a corrosion system or environment, thus allowing the reaction to continue. Such a system requires an anode or oxidizing area, where

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base metal is transformed to metallic compounds, and a cathode or reducing area, where metal is precipitated, gas evolved or other similar chemical reaction occurs to compensate for the anode reaction. These electrodes must be immersed in a common conducting fluid or electrolyte and connected together electrically for the passage of electric current.

Acid attack may be considered as being one or more of these and occurs in two varieties: non-oxidizing acids, such as hydrochloric, react rapidly with or without the presence of oxygen, evolving hydrogen gas from the cathode; oxidizing acids, such as nitric, react by reduction of the oxidizing agent at the cathode, instead of evolving hydrogen.

Corrosion, like many natural phenomena, fortunately exhibits the duality principle of action and reaction, whereby the corrosion reaction produces conditions or substances which tend to stop or impede it. Two types of this manifestation provide us with useful tools for combating corrosion: inhibition and passivity.

Inhibition is the stifling or smothering of an active corrosion surface by the yielding of sparingly soluble corrosion products. A substance which, when introduced into the electrolyte, promotes this condition is an inhibitor, called anodic or cathodic according to which surface it tends to smother or inhibit.

Anodic inhibitors are the more common and are generally quite effective. They are, however, somewhat dangerous, in that if present in insufficient quantity completely to blanket the anode area, they intensify the attack on the unprotected areas, such as corners, crevices, under deposits of sludge, etc., and result in deep and rapid pitting. Commonly used anodic inhibitors are carbonates, phosphates, silicates and chromates.

Cathodic inhibitors are considered less efficient than the anodic type, but can be used safely, since they do not dissolve the cathode material, but by reducing the cathodic area tend to minimize the overall reaction and spread it over a relatively large anode surface. The outstanding example of cathodic inhibition is the use of calcium bicarbonate to protect steel pipe conveying hard natural waters. The

cathodic reaction raises the pH and deposits $CaCO_3$ which reacts with the iron salts from the anodic reaction to form a protective coating over the pipe surfaces. Unfortunately, cathodic inhibitors, although very good, are quite rare. Some pickling inhibitors are said to be cathodic and quite possibly some of the properties of the hexametaphosphate glasses may be cathodic in nature.

Passivity is a condition commonly defined in two ways:

1. When a metal active in the EMF series exhibits an electrochemical behavior of a less active or more noble metal.
2. When a metal resists corrosion in an environment where thermodynamically there is a large free-energy decrease, associated with the appropriate corrosion activity.

Without getting overly involved in theory, passivity is generally attributed to the existence of a film of oxide, gas, or other material which resists attack and protects the underlying metal from attack. It has also been found that a highly passive metal can often impart its protective characteristics to other metals with which it will form a solid-solution alloy. Thus, chromium and nickel impart their characteristics to the base metal, iron, to form the so-called stainless-steel alloys.

Passivity occurs naturally to some extent in many instances, such as the films of oxide on iron or aluminum. However, it is induced or intensified by treatment, such as exposing iron to concentrated nitric acid, sodium nitrite or potassium dichromate, or lead to sulfuric acid, or aluminum to sodium silicate.

In general, passivity is favored by oxidizing conditions and destroyed by reducing conditions. It is destroyed by halogen ions, such as chlorides; hence, stainless steels are not particularly useful in chloride environments. Passivity on amphoteric metals, such as aluminum, is also destroyed by alkalis.

This discussion of corrosion fundamentals may be closed with the observation that, in general, corrosion is favored by increases of oxygen, carbon dioxide, acidity, temperature or velocity. Generalizations, however, are dangerous, particularly in the field of water chemistry, and should only be used as a guide for observation.

In the specific field of fresh water corrosion, environment is usu-

ally more important than minor changes in materials of construction. It is on this premise that most corrective measures are predicated.

The outstandingly bad actors in water corrosion are dissolved oxygen and carbon dioxide. In many cases, oxygen by itself tends to passivate metal surfaces, but this passivity is destroyed by the presence of CO_2, permitting the oxygen reaction to proceed unhampered. This is especially apparent in the corrosion of steam-condensate conductors. As other impurities appear, particularly in hard waters, the activity of the oxygen-carbon dioxide combination tends to diminish, but over-all corrosive effects may become more complex.

Another corrosion mechanism which frequently occurs in oxygen-deficient waters is the reduction of sulfates by bacteria, resulting in the oxidation of metal surfaces. The obvious correction to this problem is the destruction of the bacteria, usually by chlorination. This condition is frequently observed in waters from deep wells and is usually characterized by noticeable presence of hydrogen-sulfide odor from the water.

Another important mechanism of corrosion is that of differential aeration cells. These tend to localize attack in oxygen-deficient areas in cracks, crevices, etc., while other areas are exposed to aerated solution. In such reactions the oxygen-deficient areas become anodes. This usually accounts for water-line corrosion where an initial cathodic reaction, due to high oxygen content on the surface, tends to precipitate insoluble compounds, which subsequently mask the underlying metal, to isolate the surface from oxygen exposure and form an active anode.

The differential aeration-cell type of attack is intensified by insufficient addition of anodic inhibitors as previously discussed, particularly when chlorides are present.

The most common manifestation of the foregoing corrosion processes on iron and steel in fresh water media is tuberculation, the familiar mounds of corrosion products covering anodic areas where active pitting is taking place. These tubercles are covered with a red shell of ferric oxides, within which is a porous mass of black ferrous oxides.

The tubercles promote corrosion in several manners: differential aeration cell, by shielding the underlying area from oxygen penetration; concentration of the negative ions, such as chlorides and sul-

fates, with consequent lowering of pH into the acid range; and frequently by harboring anaerobic bacteria.

Tubercles apparently undergo both active and passive periods, such that after a period of active build-up, the action will stop and allow other tubercles to grow over the uncovered areas of the metal. Thus, in time there is a more or less uniform build-up of corrosion masses, which is sometimes more objectionable than the corrosion itself, particularly in pipe lines, which sometimes become completely blocked.

Another common manifestation of fresh water corrosion is dezincification of brasses, which, as the name implies, is the removal of zinc from the alloy, leaving a porous plug of spongy copper. This is evidenced by the slow escape of water through the affected areas, which upon evaporation sometimes leave considerable deposits of precipitated water solids. The usual cause of dezincification is excessive carbon dioxide in the water.

Cavitation, although not normally encountered in water systems, is usully a combination of mechanical and chemical attrition, which on occasions becomes surprisingly severe. It is usually observed in the vicinity of high-velocity fluids, such as ship propellers, pump impellers and, in some cases, vapor condensers. The mechanical action associated with cavitation is essentially the rapid formation and collapsing of voids, which set up extreme mechanical stresses similar to water hammer and which actually deform the surface metal to the extent of throwing off minute metal particles. When this occurs in a corrosive medium, protective films become almost non-existent and uninhibited corrosion greatly hastens the process of destruction.

Most other types of corrosion in water systems are characterized by just plain solution of metals or by pitting with some surrounding accumulation of insoluble solids. These conditions are usually detectable by taste, by staining or sometimes by unannounced failures, particularly by the higher metals such as copper.

Water-corrosion problems vary with the types of systems in which the water is contained. Water conductors, such as mains, hot and cold domestic water systems, and to a large extent steam boilers, are characterized by constant exposure to the corrosive properties of the water supply. Thus an objectionable condition must be remedied,

either by providing materials of construction which will withstand the attack or by continuous treatment of the water supply to reduce its corrosive action. Both are common. Where corrosion of major cast-iron and steel lines becomes a problem, the only economic solution is treatment of the water. However, most water supplies, whether treated or not, become somewhat corrosive when heated; hence, most domestic hot-water systems are piped in brass or copper.

Generally the treatment of natural waters consists of maintaining a slightly alkaline condition at about pH 8 or adjustment of the carbonate balance to maintain an excess of calcium carbonate. The first consideration and greatest problem in such treatment is economics, and where the water is intended for potable use, no toxic substances can be tolerated.

Where economically justified, sodium-silicate treatment to the extent of about 8 ppm has been found harmless to domestic use and has greatly reduced the tuberculation of steel, dezincification of brass, and corrosion of copper, led and aluminum. Also the hexametaphosphates (Calgon) in proportions up to 8-10 ppm, either alone or in combination with silicate, have been found to retard corrosion, prevent formation of scale deposits from calcium and magnesium, and prevent discoloration by dissolved iron. Organic inhibitors, although sometimes efficient, are too expensive for general treatment of this sort.

Closed systems, such as hot-water heating systems and fire-protection sprinkler systems, present few problems, inasmuch as the normal corrosive elements present are quickly consumed and corrosion ceases. In heating systems, however, hydrogen is formed from whatever corrosion does take place and must be vented. Maintaining a pH of 8.5 will stop this nuisance.

Open recirculated systems, such as spray ponds, etc., are usually inhibited by maintaining sodium chromate at 300 ppm and pH 8.5. Chromate is probably the most generally used of these inhibitors because of its effectiveness and ease of control by colorimetric methods. As mentioned previously, chromates have the disadvantages of being anodic inhibitors, toxic, and subject to depletion through reduction by certain organic matter such as alcohols. Organic inhibitors are sometimes used, but are usually expensive and highly proprietary.

Storage tanks are best protected by cathodic methods, either by use of electrical rectifiers or by sacrificial anodes. In this application, the required protective current may be greatly reduced by protective coatings on the tank surfaces.

The protection of steam boilers, being a very critical service, has become a highly specialized enterprise. Of great importance is the absolute exclusion of oxygen from the feed water. This is usually done with deaerators, followed by a chemical scavenger, such as sodium bisulfite, to remove the last traces of oxygen. To some extent, organic scavengers, such as cyclohexylamine, are used with the aerators or alone.

Generally speaking, three principles are observed in the prevention of boiler corrosion: (1) maintain alkalinity at pH 11-12; (2) exclude oxygen; (3) keep boiler surfaces clean.

Also necessary in the treatment of boilers, though not for purposes of corrosion, is the use of phosphates to engage the calcium and magnesium salts, to prevent the formation of insoluble scale on the heating surfaces.

Several references are available for corrosion data. A great deal of corrosion work is carried on by various agencies and reported in several technical journals; outstanding are:

"Corrosion," published by the National Association of Corrosion Engineers.

"Metals Preview"—monthly publication by the American Society for Metals, containing abstracts of corrosion articles.

"Chemical Engineering"—monthly publication by McGraw-Hill, with an active corrosion subsection.

Among the standard text references are the excellent corrosion handbook by Professor Uhlig, M.I.T., and, for specific information on corrosion rates versus concentration, temperature, etc., the Shell Corrosion Handbook, published by Shell Chemical Corp.

Much industrial literature is available from metals manufacturers, such as International Nickel Corp. and the various steel companies. There is also a great profusion of literature for proprietary anti-corrosion materials, but these are not recommended for general reference.

CORROSION CONTROL WITH METAPHOSPHATE GLASS

BY JAMES C. LAMB, III,* AND ROLF ELIASSEN†

[*Read January 21, 1954.*]

Past Work

Sodium metaphosphate glasses were first used in the waterworks field for preventing scale formation. Early investigators found that the addition of small quantities of these chemicals to waters prevented the precipitation of calcium carbonate, corrosion products and certain other scale-forming compounds. It was felt that the precipitation of calcium carbonate was stopped on the threshold of crystallization. For this reason, the term "Threshold Treatment" was applied to this process.

In 1939, Hatch and Rice (1) stated that metaphosphate was of value as an aid in the control of corrosion. This was based on the feasibility of raising the pH of metaphosphate-treated water to a very high value without incurring the deposition of calcium carbonate. It was observed that Threshold Treatment not only prevented the deposition of calcium carbonate in pipelines, but slowly removed old deposits from the metal (1, 2). In many distribution systems a layer of calcium carbonate on the internal surfaces of pipelines served to protect the metal from the corrosive action of water. The removal of this protective coating by metaphosphate was the cause of great concern to many members of the waterworks profession.

Field investigations revealed that the rates of corrosion in systems stripped of calcium carbonate coatings by metaphosphate had not increased as anticipated. The pipelines in these systems were found to be in excellent condition, in spite of the apparent lack of protection. In 1939, on the basis of field and laboratory studies (3), Rice and Hatch concluded that metaphosphate itself had an inhibitory effect on corrosion. The inhibitory action was attributed to the formation of an adsorbed film of metaphosphate on the metal surface. This film

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was found to be so thin that its presence could be detected only through the formation of "Interference Colors" on the metal.

Since 1939 many laboratory and field investigations have been conducted on the corrosion-inhibiting properties of metaphosphates (4-38, 46, 47). The earlier studies (4-22) were undertaken for the purpose of evaluating the effectiveness of metaphosphates in reducing corrosion. Although negative results were obtained in some instances, a review of the extensive literature revealed that these chemicals were found to be effective corrosion inhibitors in an overwhelming proportion of the field applications. It is significant that most of the unfavorable conclusions were based upon laboratory or pilot-plant results, obtained under conditions basically different from those found in practice. Possible reasons for the seemingly strange behavior of metaphosphates under laboratory conditions will be discussed later in this paper.

In recent years it has become increasingly apparent that the inhibitory action of metaphosphate is of a complex nature. Several individuals have investigated the mechanism by which these chemicals inhibit corrosion (23-29, 46, 47). As in the earlier investigations, conflicting conclusions were drawn relative to the action of metaphosphates. The literature survey revealed once again that these chemicals appeared to be affected radically by the laboratory conditions under which the tests were conducted.

In 1940, Hatch and Rice (4) stated that the inhibitory action was due to the formation of a protective film of metaphosphate on the metal surface. Little explanation was offered of the exact mechanism through which this film was deposited. Later investigators have classed metaphosphate as an anodic inhibitor (30-32), a cathodic inhibitor (23-28, 32a, 41), or a mixed inhibitor (47).

In 1950, Mansa and Szybalski (23, 24) investigated the effects of metaphosphate on corrosion of iron in differential aeration cells. It was concluded that large molecules of Calgon, or its complexes, were adsorbed on exposed cathodic areas. The inhibitive action of the chemical was attributed to the formation of this protective cathode film and the resulting reduction in the potential of that electrode. Therefore, these authors concluded that metaphosphate should be classed as a cathodic inhibitor.

In 1952, Hatch (25, 26) likewise stated that this chemical should be considered a cathodic inhibitor. On the basis of laboratory investigations, it was concluded that a protective film of calcium metaphosphate complexes was formed on the cathodes of corrosion cells through electrodeposition.

In 1952, Raistrick (27) stated that a protective layer of calcium carbonate was formed on the cathodes of corrosion cells. He postulated that the inhibitory action of metaphosphate could be attributed to adsorption of the chemical on this calcium carbonate layer, preventing it from passing into solution. Under these conditions, the primary role of metaphosphate would be to stabilize the protective film of calcium carbonate on the surface of cathodic areas of metal.

In 1946, Evans (40) classified metaphosphate as a "dangerous" inhibitor, on the basis of unpublished results. Later, in 1951, this author (32a, 41) referred to the work of Mansa and Szybalski, and stated that Calgon probably should be considered as a cathodic inhibitor. The possibility of colloidal action by this inhibitor was mentioned, but no data were presented at that time.

In 1955, Uhlig, Triadis and Stern concluded that in the presence of oxygen these chemicals were mixed inhibitors (47). This was based upon formation of a diffusion barrier on cathodic areas by calcium polyphosphates, and passivation of the metal through chemisorption of oxygen on anodic areas. It was concluded that Raistrick's proposal (27) was not tenable.

Since these chemicals are widely used in the waterworks field, it is highly important that their effects on pipeline corrosion be evaluated. It has been pointed out that past investigators have experienced great difficulties in attempting to obtain accurate and consistent results from laboratory studies of these inhibitors. In order to obtain accurate information from laboratory corrosion tests, it is necessary that the variables affecting the action of the inhibitors be understood and properly controlled. It is impossible to evaluate all of the variables affecting an inhibitor until the basic inhibitory mechanism is understood. This paper reports on part of the extensive investigation which was undertaken to find the basic mechanism by which metaphosphates inhibit the corrosion of iron in water and to interpret this mechanism in terms of practical waterworks problems.

Corrosion of Iron in Natural Waters

The corrosion of iron in water results from the formation of anodes and cathodes on the surface of the metal. Some of the typical half-cell reactions, which are generally considered (40, 42, 43, 45) to occur at the individual electrodes of corrosion cells, are shown in Figure 1. These half-cell reactions have been discussed in more detail

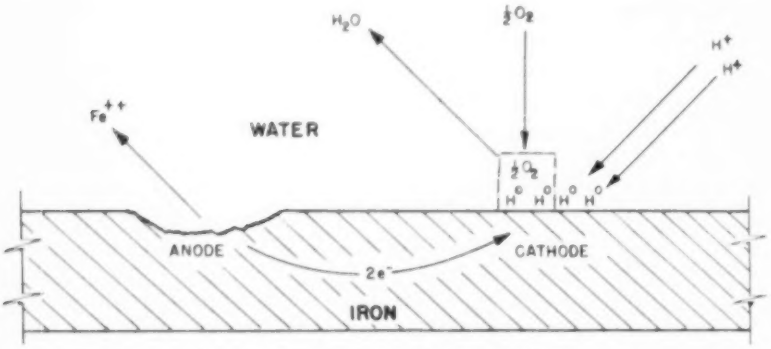

FIG. 1.—CORROSION CELL—IRON IN WATER.

by Camp (39). The surface of a large section of metal would be covered by a great number of corrosion cells, with similar reactions occurring in each. The initial formation of anodes and cathodes on a submerged metal may be due to differences in metal composition, electrolyte concentration cells, differential aeration cells, or differential temperature or stress cells (39, 42).

In the corrosion cell shown in Figure 1, it is seen that iron passes into solution at the anode, leaving electrons on the metal. These electrons pass through the metal to the cathode area, where they may be removed from the iron through reaction with hydrogen ions in solution, producing atomic hydrogen, or by one of many other half-cell reactions which depend on the substances present in the vicinity of the cathode and on the relative energies governing half-cell reactions. Under certain conditions the hydrogen atoms tend to plate out on the metal. Unless removed they will interfere with the transfer of other electrons to solution. Within the pH range normally found in water-

works practice, it is generally considered that the primary mechanism through which hydrogen is removed from the cathode is by reaction with dissolved oxygen in the water (oxygen depolarization), as shown in Figure 1 (42, 43).

The rate of corrosion is a function of the rate of electrical current flow between anodes and cathodes on the surface of a metal (42). It is evident that in order for corrosion to take place (anode reaction), the electrons left on the metal by this reaction must be removed (cathode reactions). Otherwise, a counter E.M.F. will be built up on the metal. This will oppose the anode reaction and corrosion will be stifled. Therefore, the anode and cathode reactions in a corrosion cell must proceed at the same rate. Any reduction in the rate of either reaction must result in a corresponding reduction in the rate of current flow between the electrodes, and hence in the rate of corrosion. In practice, the rate of corrosion may be controlled by reducing the rate of either anode or cathode reactions, or both.

Under the conditions usually found in natural waters, the anode reaction rate is much more rapid than the depolarization reaction rate at the cathode (43). Since both reactions must proceed at the same rate, it is evident that the cathode reaction controls the rate of corrosion. Therefore, in waterworks practice corrosion is usually under cathodic control, with the rate of supply of oxygen and other oxidants to the cathode areas governing the over-all weight loss of metal to solution (42).

The Action of Inhibitors

An inhibitor is any substance which, when added in small amounts to a corrosive environment, significantly decreases the corrosion rate of a metal or alloy. The protective action of inhibitors is due mainly to the formation of films on the metal surface. These films in turn retard the corrosion reactions. The protective film may act preferentially at the anodes or cathodes of corrosion cells, or it may be adsorbed generally over the entire surface of the metal. On this basis, Evans (40) has divided inhibitors into three large classes:

(1) Anodic inhibitors
(2) Cathodic inhibitors
(3) Adsorption inhibitors

It should be pointed out that these classes are not clearly defined, since some inhibitors may act in more than one manner.

Anodic inhibitors reduce the rate of corrosion by restraining the anode reaction. The addition of an anodic inhibitor to water results in the formation of a protective film over anode areas. This protective film tends to separate the metal from the corrosive liquid and, therefore, interferes with the transfer of metal ions to solution. The addition of a sufficient quantity of anodic inhibitor to a water could result in the formation of a continuous film over the surface of the metal, almost completely stifling the corrosion reactions.

The addition of insufficient anodic inhibitor to the corrosive medium would result in the formation of only partially protective films over anodic areas. It has been pointed out previously that the rate of corrosion of iron in water is usually controlled by the rate at which the cathode reactions take place. Therefore, partial covering of the anodes would have little effect on the over-all rate at which metal passes into solution (43, 44). However, this partial shielding would result in intensification of attack on the reduced anodic areas, and rapid failure of the structure could result through pitting. For this reason, Evans (40) classified anodic inhibitors as "Dangerous" inhibitors.

It is significant to note that the rate of supply of inhibitor to the metal is not governed by chemical dosage alone. The velocity of flow, diameter and condition of the pipe interior are of great importance in bringing the inhibitor into contact with the metal. The use of reasonable dosages of an anodic inhibitor for the protection of the main lines of a distribution system could lead to an insufficient supply of inhibitor, with severe pitting resulting, in small branches and dead ends. Protection of the entire system, including pipelines with very low flows, would require extremely high inhibitor dosages. Therefore, the use of anodic inhibitors in municipal water systems would require the closest possible control.

Cathodic inhibitors reduce the rate of corrosion by interfering with the cathode reactions. These inhibitors are less efficient in reducing the over-all corrosion rate than are anodic inhibitors, when used in proper quantities (45). This may be attributed, in part, to the fact that a protective film is formed over the cathode. The film sets up a differential aeration cell, with the shielded cathode tending to be-

come anodic to the exposed anode. This results in continual changes in the locations of anodes and cathodes on the metal with corrosion continuing at a reduced rate.

The protective film formed by a cathodic inhibitor interferes with the access of dissolved oxygen to the metal surface, and reduces the effective area of the cathode. When corrosion is under cathodic control, any reduction in the effective cathode area must result in a corresponding reduction in the over-all corrosion rate. A true cathodic inhibitor would not decrease the effective anode area. Therefore, the addition of a reasonable dosage of a cathodic inhibitor to a municipal water supply would result in less than optimum action of the inhibitor in pipelines with very low flows, but would not cause intensification of attack. Evans (40) has classified cathodic inhibitors as "Safe" inhibitors, since insufficient supply would not be expected to lead to pitting attack.

Some organic substances appear to be adsorbed generally over the entire metallic surface (40). These compounds may be classed as adsorption inhibitors, and they may interfere with either or both electrode reactions.

The action of corrosion inhibitors may be illustrated as in Figure 2 (40, 42, 43, 45). The solid lines in this figure are typical polarization curves for the anode and cathode of a corrosion cell. The corrosion current and corrosion potential of the cell, in the absence of inhibitors, are shown by the intersection of the anode and cathode curves at point 1. This point represents the conditions prevailing when the electrodes are short-circuited, which is usually the case in practice with both electrodes located on a single piece of metal. It will be noted that the slope of the cathode curve is much greater than the slope of the anode curve. Since the rate of corrosion (corrosion current) in this cell is limited by the change in potential, or polarization, of the cathode with increased current flow through the cells, the corrosion is said to be under cathodic control. It has been pointed out that this is the situation which is usually found in waterworks practice.

The addition of an anodic inhibitor to this system would result in increased polarization of the anode, as shown by the dotted line passing through point 2. The increase in the degree of polarization is shown by increased slope of the anode line, indicating a greater change

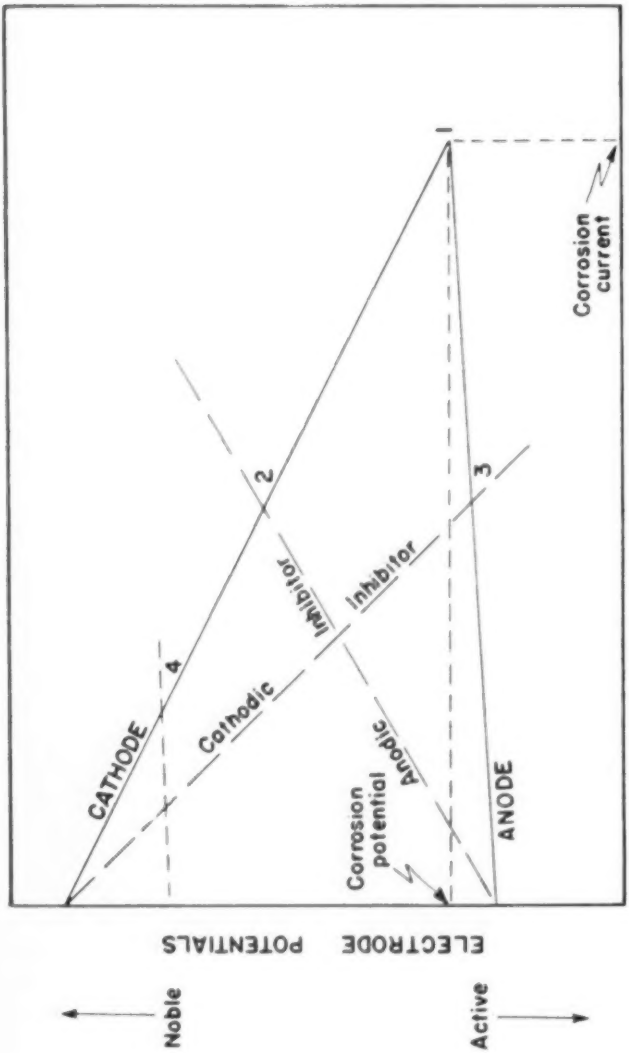

FIG. 2.—THE EFFECTS OF CORROSION INHIBITORS ON THE POLARIZATION OF ANODES AND CATHODES

in anode potential for a given change in electrical current flow through the cell. With a purely anodic inhibitor, the curve for the cathode would remain unchanged, giving new polarization curves for this cell as indicated by the lines intersecting at point 2. Comparing points 1 and 2 reveals that the addition of the inhibitor resulted in a decrease in the corrosion rate in the cell, and a more noble corrosion potential.

The addition of a cathodic inhibitor to the water would result in new polarization curves similar to those represented by the lines intersecting at point 3. These curves indicate that the inhibitor caused an increase in the degree of polarization of the cathode, resulting in a corresponding reduction in current flow, or corrosion rate, and a less noble corrosion potential.

The addition of an inhibitor to a corroding system may have an added effect on polarization curves which is not indicated by the curves intersecting at points 2 or 3. The inhibitor may cause a change in the open-circuit potentials of either or both electrodes. For example, the addition of a passivating agent could result in a more noble open-circuit potential of the anode. Examination of Figure 2 shows that a displacement of the entire anode curve in the noble direction, with or without increased slope of the curve, would result in a reduced value of current flow at the intersection of the anode and cathode curves. This is illustrated at point 4 in Figure 2.

Experimental Equipment

The importance of velocity in determining the rate of corrosion of iron in water has been known for many years (40, 42, 43, 45). It has been found that the effect of velocity is even more pronounced in metaphosphate-treated waters. In untreated water the rate of corrosion tends to increase with increase in velocity, due to the more rapid rate of supply of oxygen to the metal surface. In water to which metaphosphate has been added, increase in velocity up to some critical value results in a net reduction in the rate of corrosion, in spite of the increased rate of supply of oxygen to the metal (16). This may be attributed to the increased rate of supply of inhibitor to the metal surface.

Since there is little or no control over velocity in most batch testing procedures, these tests should be used with extreme caution in

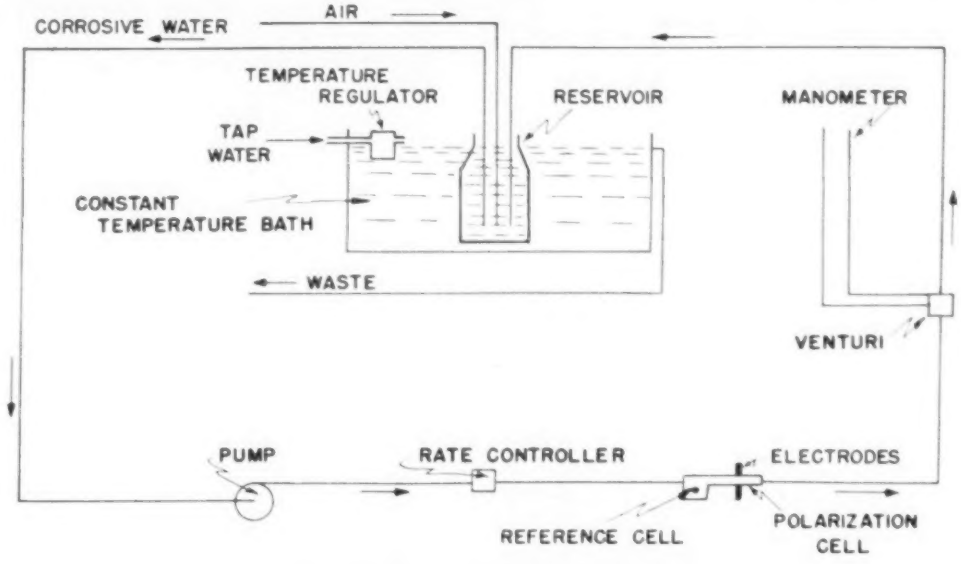

FIGURE 3 - FLOW DIAGRAM

attempting to evaluate the action of metaphosphate as a corrosion inhibitor. Another limitation of the use of small-volume batch tests for investigating the action of metaphosphate is that the total amount of inhibitor available to the metal is limited to that present in the beaker. Under continuous flow conditions there is a constant supply of inhibitor to the metal, and the amount of chemical available per unit area of metal surface may be very large over a long period of time.

In view of the above considerations, the experimental equipment used in the initial phase of these studies was of the continuous flow type. A flow diagram of this equipment is shown in Figure 3. A five-gallon glass carboy was used as a reservoir for the corrosive water. This reservoir was immersed in the constant temperature bath which was maintained at 27° C ± 1°, and the oxygen content of the corrosive water was maintained at a constant value through continuous aeration. The corrosive water was circulated in the test system by means of a stainless steel centrifugal pump, and the rate of flow was regulated with "C" clamps located on the discharge side of the pump. From the pump the water passed through lucite cells which held the electrodes serving as test specimens. The rate of flow of the water in the system was determined by means of a Pyrex venturi tube, connected to manometers as shown in the flow diagram. All pipes in the system were made of Pyrex tubing or rubber hose. The corrosive water did not contact any metal in the test system, with the exception of the stainless steel pump and the corroding specimens.

Figure 4 shows the details of contruction of the special lucite cell used in polarization studies. The material used for fabricating the main body of this cell was ¼-inch lucite sheet. Two-inch sections of 1¼-inch lucite tubing were welded to opposite sides of the cell, as shown, and 1-inch holes were drilled in the sides of the cell, concentric with the lucite tubing. A saturated calomel reference electrode was mounted in the cell as shown in Figure 4. Waterproofing was accomplished by passing the reference electrode through a tightly fitting rubber stopper.

The specimens used in this cell were machined from 1-inch round bar stock. The finished specimens had a length of approximately five inches, and a diameter of 0.975 inch. The end of each bar was finished as a corrosion specimen, following approved techniques. All of the

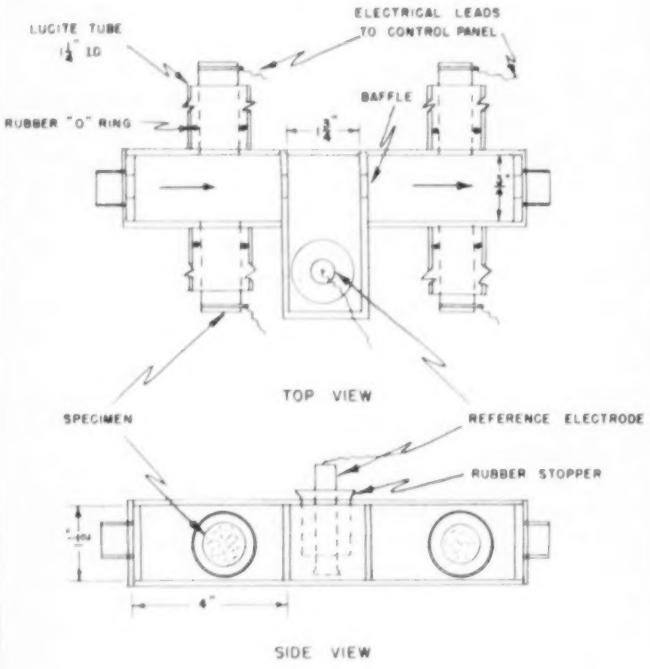

FIGURE 4

POLARIZATION CELL AND SPECIMENS

metal except for the finished end of the bar was waterproofed by wrapping the specimen tightly with Scotch Electrical tape. The specimens were mounted in the cell with rubber "O" rings, which were rolled into place between the metal and the lucite tubing. The corroding surfaces were mounted flush with the internal surfaces of the lucite. Therefore, the electrodes of the galvanic cells faced each other across the channel of flowing water, separated by a distance of ¾ inch.

Galvanic cells of steel and stainless steel were used in this study to facilitate analyses of the action of metaphosphate on the individual electrodes in a corrosion cell. The use of galvanic cells resulted in partial separation of anodes and cathodes, and the use of stainless steel cathodes minimized the introduction of foreign metal ions into the test solution. The action of metaphosphate on the separated electrodes of galvanic cells of this type should be similar qualitatively, but not quantitatively, to its action on electrodes located on the surface of a single piece of metal. This concept is correct, provided that the action of the inhibitor does not involve direct chemical reaction between the inhibitor and the metal to a significant extent. This possibility will be discussed further in a later section.

The wiring diagram of the electrical equipment used for polarization measurements is shown in Figure 5. All anodes and cathodes in the corrosion cells under test were connected to banana plug jacks on a central control panel. When measurements were not being made, the incoming anodes and cathodes were shot-circuited at the panel by means of the switches shown between the banana plug jacks. The leads from the reference cells were connected to a rotary switch, and through this switch to one side of the electrometer.

A "Zero Resistance" ammeter (45) was used to measure the short-circuit current flowing between the electrodes of the galvanic cells. Short sections of wire (jumpers), with banana plugs on each end, were used to connect the incoming anode and cathode into the zero resistance ammeter circuit. The current flow in the auxiliary 1.5-volt circuit was adjusted by means of the three rheostats until the galvanometer showed no deflection with the key depressed. When this balance was attained, the current flow in the auxiliary circuit produced an IR drop through the 100-ohm resistance which was equal and opposite to the IR drop through the microammeter. Under these

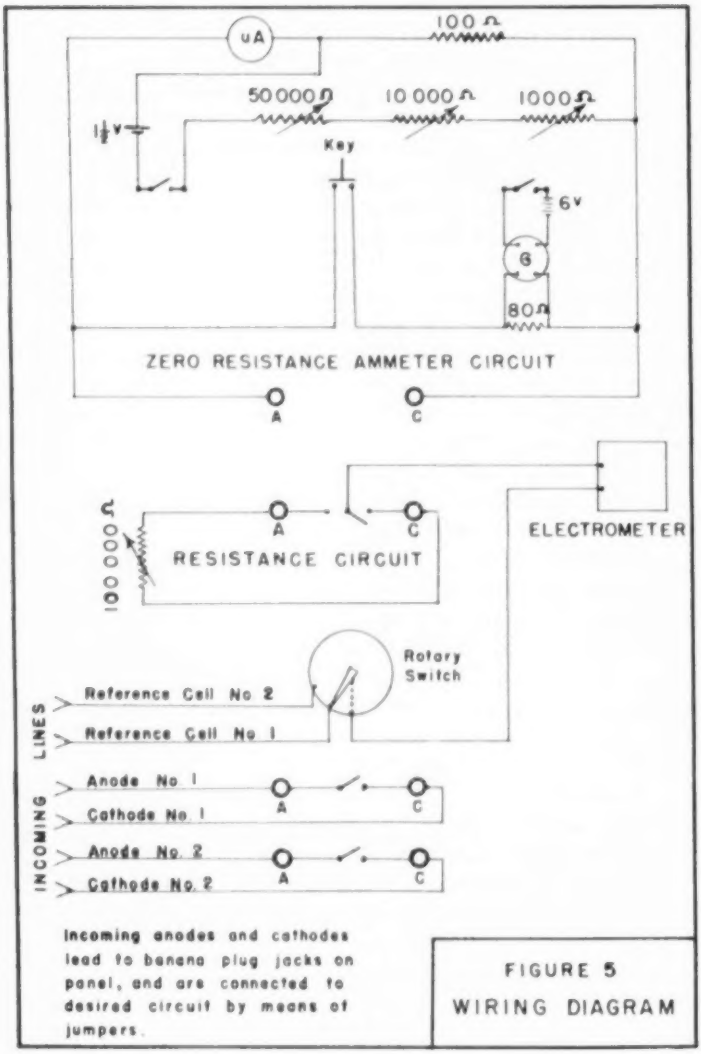

FIGURE 5
WIRING DIAGRAM

conditions the potentials of the anode and cathode were equal, or in effect the two electrodes were short-circuited. The value of the short-circuit current was read directly on the microammeter.

In order to measure the polarization characteristics of the electrodes in the galvanic cells, it was necessary to introduce various resistances between the electrodes, and to measure the potential of each electrode against that of the standard reference cell. This was accomplished by connecting the incoming anode and cathode to the "Resistance Circuit" by means of jumpers. The resistance between the electrodes during measurements was controlled by means of a 100,000-ohm decade resistance. A switch located in the resistance circuit made it possible to connect the electrometer to either the anode or cathode. The other side of the electrometer was connected to the proper reference cell through the rotary switch. This arrangement permitted rapid measurement of the anode and cathode potentials, with any desired resistance between the electrodes.

It was necessary to prevent variations in the chemical characteristics of the corrosive waters during the several runs. Therefore, a synthetic tap water was prepared with distilled water and reagent grade chemicals. The chemical composition of this water is shown in Table 1. The water was dosed with 10 ppm of chlorine at the beginning of each run to minimize biological activity. The chlorine residual was dissipated within 12 hours after beginning the run. The pH of the water was approximately 8.0, and the velocity through the specimen holder was adjusted to 1.0 foot per second.

TABLE 1. COMPOSITION OF SYNTHETIC TAP WATER

Chemicals Added		Resulting Ions — ppm					
Chemical	ppm.	Mg^{++}	Ca^{++}	Na^{+}	Cl^{-}	SO_4^{--}	HCO_3^{-}
$MgSO_4$	34.65	7.00				27.65	
$CaSO_4$	27.09		7.98			19.11	
$CaCl_2$	39.12		14.12		25.00		
$NaHCO_3$	96.30			26.36			69.94
Total Ionic Concentrations		7.00	22.10	26.36	25.00	46.76	69.94

Metaphosphate Film Formation

The initial phase of this investigation was devoted to a study of the deposition of metaphosphate on anodes and cathodes of galvanic cells as a function of time under continuous flow conditions. It was found that the quantities of metaphosphate deposited on the test electrodes usually were very small. Radioactive metaphosphate glass, used in conjunction with special removable specimens, made it possible to determine the amounts of metaphosphate deposited without removing the protective films from the metal. The equipment, procedures and results of these radioactive tracer experiments have been reported in detail in other papers (28, 29).

The anode deposits of metaphosphate varied erratically, and were in the order of 20 to 100 times as great as the amounts of metaphosphate deposited on the cathodes. Subsequent studies revealed that the smaller deposits on the cathodes were responsible for the inhibitory action of the metaphosphate. Small quantities of corrosion products in solution were found to enhance the deposition of metaphosphate on cathodes. Subsequently it was found that the protective film contained corrosion products in addition to metaphosphate and possibly other chemicals. It was concluded that the inhibitory action could not be related solely to the amount of metaphosphate deposited on the cathodes, since this chemical was only one constituent of the protective film.

In view of the fact that corrosion products were found to increase metaphosphate film formation, the next step in this investigation was to study their effects on the inhibitory action of this chemical.

Electrical Current Flow

The rate of electrical current flow between the electrodes of a galvanic cell is a measure of the corrosion rate due to galvanic action. As pointed out in the preceding section, the presence of corrosion products in solution enhanced the deposition of metaphosphate on cathodes. The studies reported in this section were undertaken for the purpose of determining whether corrosion products exerted any effect on the inhibitory action of metaphosphate.

The basic equipment and testing conditions have been described previously, except for a specimen holder which was introduced into

the continuous flow system in series with the "Polarization Cell." This specimen holder was designed to hold eight galvanic cells. The use of baffles resulted in the formation of eight compartments, each of which was identical to the compartments in the polarization cell described previously. Also, the location of the electrodes in each compartment was identical with their location in the polarization cell. This caused flow conditions in the vicinity of the two electrodes of all galvanic cells which were similar to those encountered in the polarization cell. This device has been described in detail in a preceding paper (28). The electrodes on opposite sides of the specimen holder were normally short-circuited by means of short sections of wire to form galvanic pairs.

A zero resistance ammeter was used to measure the galvanic currents, since the introduction of even a low resistance microammeter in the circuit between the electrodes would have a significant effect on the magnitude of the corrosion current. The wire connecting the anode and cathode was disconnected and the electrodes were connected to the zero resistance ammeter. After measurement of the galvanic current with this instrument, the electrodes were immediately short-circuited again.

Since the specimens used in these runs were pickled in acid, and had a very high initial corrosion rate, it was desirable to use higher dosages of metaphosphate than those usually employed in practice. Hatch and Rice have shown in several papers that laboratory results obtained with 50 ppm of metaphosphate are qualitatively similar to results obtained with 2 to 5 ppm in practice. Therefore, the use of 50 ppm of metaphosphate during these studies is justified as long as no attempt is made to evaluate the quantitative efficiency of the inhibitor on the basis of the test results.

Two sets of parallel runs were made, using the two continuous flow systems. In the first set of runs 0.5 ppm of iron powder was added to the water of system number 1 and no iron was added to system number 2. In the second set of runs the procedure was reversed to eliminate any possible variations in the operating characteristics of the two systems. The iron was added in the form of powder to introduce it into solution in the same manner as when entering from the face of a corroding metal. The iron and 50 ppm of meta-

phosphate were added to the reservoir of synthetic tap water 24 hours prior to beginning the runs.

The results obtained in the two sets of parallel runs are shown in Figure 6. Each curve in this figure represents the average of the results obtained in corresponding runs in the two continuous flow systems. The curves for the individual runs were obtained by averaging the current flow measurements for the several galvanic cells in each system. The individual curves showed the same trends as are shown by the average curves presented in Figure 6.

The curves in Figure 6 reveal that the addition of iron powder to the corrosive water had a beneficial effect on the inhibitory action of the metaphosphate. It will be noted that towards the ends of the runs, the curve representing the current flow in the systems to which no iron was added tends to approach the curve for the systems to which iron was added. This can be interpreted in the light of continued corrosion of the specimens, resulting in further addition of corrosion products to the solution.

Although the data in Figure 6 show that iron had a significant and beneficial effect on the action of metaphosphate glass, the test results do not reveal the mechanism by which the iron increased the effectiveness of inhibition. The next phase of this investigation was undertaken for the purpose of ascertaining the mechanism through which iron in solution increased the inhibitory action of metaphosphate; that is, whether the increased inhibition was due to action at the cathodes or anodes of the corrosion cells.

Polarization Studies

The significance of polarization data in investigating the action of a corrosion inhibitor has been discussed previously. The studies conducted in this phase of the research were undertaken for the purpose of determining the mode of action of metaphosphate glass as a corrosion inhibitor, and the effects of iron in solution on the inhibitory action.

Galvanic couples of steel and stainless steel, mounted in the polarization cell (Figure 4), were used as corrosion specimens. Electrical leads from the anodes and cathodes were connected to banana plug jacks on the control panel (Figure 5). The electrodes of the galvanic

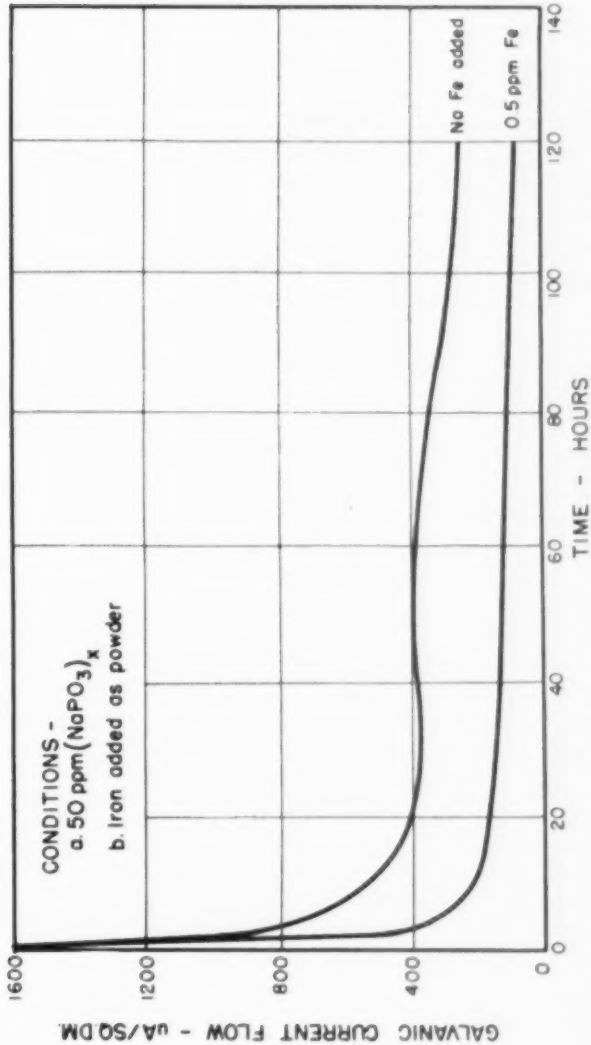

FIG. 6.—THE EFFECT OF IRON ON THE INHIBITION OF GALVANIC CURRENT FLOW BY METAPHOSPHATE.

cells were short-circuited at the control panel throughout the runs, except when measurements were actually being taken.

The corrosion potential was determined by connecting the short-circuited electrodes to the resistance circuit, and measuring the difference in potential between the galvanic cell and the standard reference electrode. The corrosion current was measured by means of the zero resistance ammeter. The location of other points on the polarization curves were determined with the electrodes connected through the resistance circuit. A desired resistance was introduced between the electrodes, and the potential of each was measured against that of the reference cell. With the potential difference and resistance between the electrodes known, it was possible to compute the current flow through the cell from the equation: $E = IR$. The shapes of the polarization curves were determined by repeating this procedure with several progressively larger resistances in the circuit. The open-circuit potentials were determined by disconnecting the electrodes, and measuring the potential of each electrode against that of the reference cell. After completing the set of measurements, the electrodes were again short-circuited.

Figure 7 shows polarization curves which were obtained under continuous flow conditions with no metaphosphate in the corrosive water. Polarization curves were obtained at several times other than those indicated in Figure 7. However, for the sake of clarity, only three sets of curves have been reproduced in this figure. In each case, the upper curve represents the potential of the stainless steel cathode at the indicated rate of current flow between the electrodes. The lower curve shows the potential-current characteristics of the steel anode. The rate of current flow at the intersection of the anode and cathode curves represents the corrosion current due to the galvanic couple. The potential at this point is the corrosion potential as measured against a saturated calomel reference electrode. The open-circuit (zero current flow) potentials of the electrodes are shown by the intersections of the polarization curves with the ordinate axis.

Examination of the curves in Figure 7 reveals that the corrosion was predominantly under cathodic control; that is, the corrosion current was limited by the degree of polarization of the cathode. This is

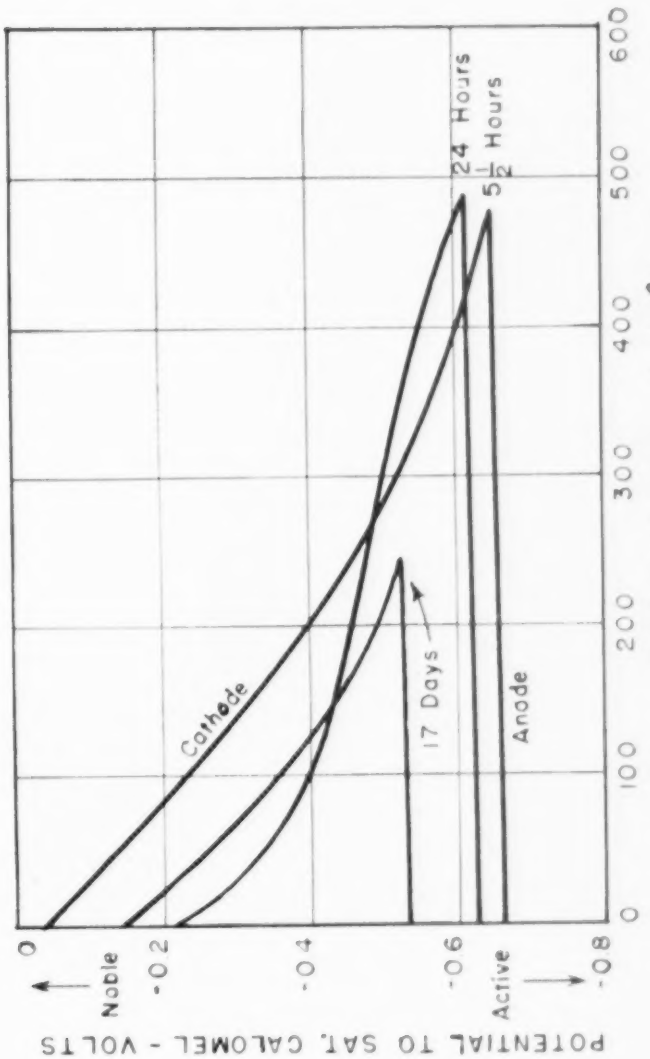

FIG. 7.—POLARIZATION CURVES—NO METAPHOSPHATE.

in agreement with established principles of the corrosion of iron in neutral or slightly alkaline waters, as discussed previously.

The open-circuit potential of the stainless steel cathode at the beginning of the run was approximately 0.08 volts noble to saturated calomel. However, the potential decreased rapidly with time to a less noble value, as shown in Figure 7. The open-circuit potential of the steel anode became more noble with time. This increased nobility of potential was probably due largely to the formation of films of corrosion products on this electrode.

After a period of 17 days, the current flow in the galvanic couple was much less than in the early hours of the run. It appears that this reduction in current flow can be attributed to the increased nobility of the anode and the decreased nobility of the cathode. These changes resulted in a smaller-open circuit potential difference between the two electrodes, and therefore a smaller driving force for galvanic current flow. There was little apparent effect on the degree of polarization of either electrode, as judged by the slopes of the polarization curves at the end of 5.5 hours and 17 days. Between these times the degree of polarization of the cathode appeared to vary, as well as the open-circuit potential of the cathode. This is shown by the polarization curves obtained at the end of 24 hours.

Figure 8 shows three sets of polarization curves obtained with 50 ppm of metaphosphate in the corrosive water. In this run, there was only one galvanic cell in the continuous flow system. Therefore, there was no source of iron in the system except for the single steel anode of this galvanic cell. Comparison of the curves in Figure 8 with those in Figure 7 reveals that the most radical change incurred by the addition of metaphosphate was a rapid shift of anode potential from a value of about 0.65 volts to a more noble value of approximately 0.45 volts. The potential of the cathode decreased at a more rapid rate in the presence of metaphosphate, but did not attain a value significantly different from the potential in the untreated system. At the end of four hours the degree of polarization of the cathode, as measured by the slope of the cathode curve, was slightly less than in the untreated system. As the run progressed, the polarization of this electrode decreased until it became significantly less than the degree of cathodic polarization in the untreated system.

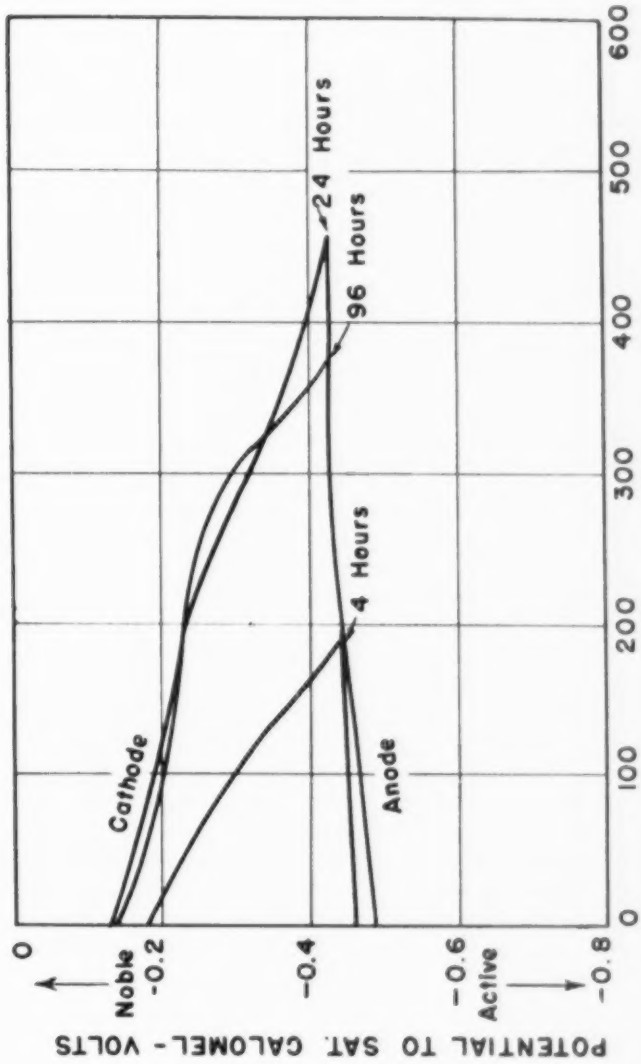

FIG. 8—POLARIZATION CURVES—50 PPM METAPHOSPHATE—ONE CORROSION CELL IN SYSTEM

Under these testing conditions, metaphosphate could not be classed as a cathodic inhibitor, as claimed by Hatch (25, 26) and Mansa and Szybalski (23, 24). The only significant changes resulting from the addition of metaphosphate to the test solution were an increased nobility of anode potential and a decrease in the degree of polarization of the cathode. This run was one of the first conducted, and did not include determination of the polarizing characteristics of the electrodes at the end of 17 days.

Figure 9 shows curves obtained under conditions identical with those in the preceding run, except that the polarization cell was mounted in the continuous flow equipment in series with the specimen holder. This was done in order to observe the effects, if any, of the additional corrosion products entering solution from the several specimens in the specimen holder. Several sets of polarization curves were obtained between 24 hours and 17 days, but these are not shown here for the sake of clarity of the figure.

The cathode potential was not changed significantly from the values obtained in the preceding run. The rapid shift of anode potential to a more noble value, which was noted in Figure 8, also occurred in this run. After this initial shift in the noble direction, the anode potential gradually decreased in the run represented by Figure 9. At the end of 17 days, the potential of this electrode had reached a value which was less noble than the corresponding anode potential in the untreated system.

The increased nobility of anode potential in the untreated system (Figure 7) was attributed to the formation of oxide films. The more rapid and greater shift in the noble direction in systems treated with metaphosphate can probably be attributed to adsorption of metaphosphate on the corrosion products. The addition of this chemical to the water evidently results in the formation of a more resistant film which causes a higher anode potential. Other investigators (4, 46) have reported that denser and more tightly adherent films were formed in the presence of metaphosphate. The gradual decrease in anode potential over a period of 17 days may be attributed to the gradual removal of corrosion products by metaphosphate. This results in the exposure of a cleaner metal surface to the corrosive solution, and a more active potential of the anode. Removal of corrosion products by

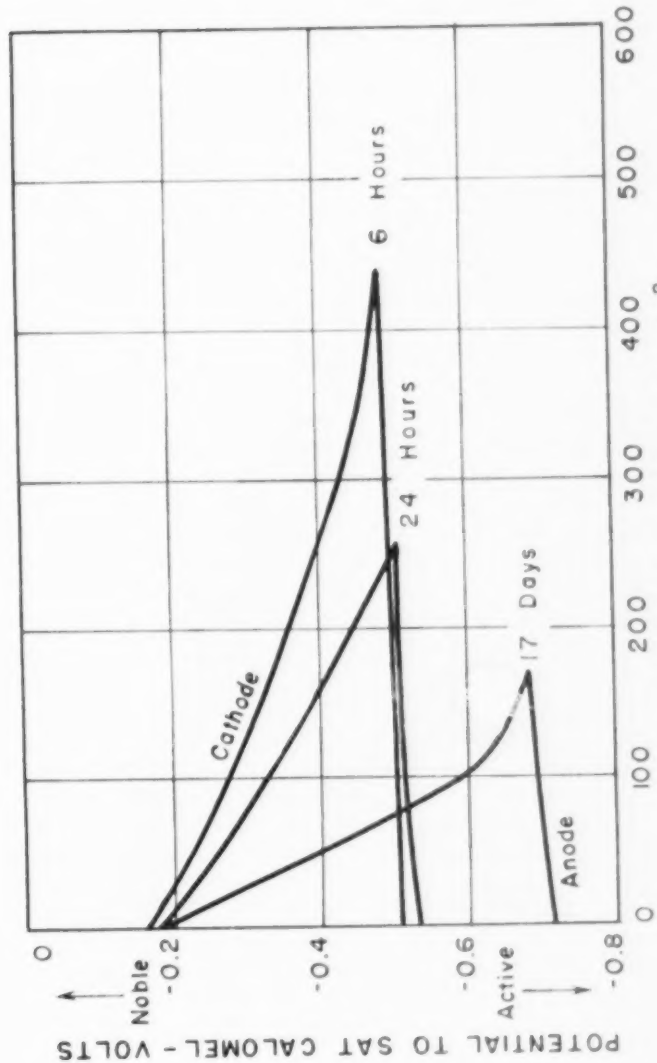

FIG. 9.—POLARIZATION CURVES—50 PPM METAPHOSPHATE—SEVERAL CORROSION CELLS IN SYSTEM.

metaphosphate over extended periods of time has been reported by many investigators, and was confirmed in these runs by visual observation of the specimens.

The current flow in the galvanic cell of Figure 9 decreased with time, in spite of the cleaning action of the metaphosphate and the increased activity of the anode potential. It is evident from the curves that the decreased current flow can be attributed to increased polarization of the cathode, as indicated by the increased slopes of the cathode curves. It is significant to note that polarization of the cathode increased in the run in which several sets of specimens were corroding; whereas in the preceding run, with only one galvanic cell in the system, no increase in polarization was observed up to 96 hours from the beginning of the run. This will be discussed more fully in a later section.

In the run represented by the curves in Figure 10 the testing conditions were identical with those in Figure 9, except that 0.5 ppm of iron powder was added to the corrosive water 24 hours prior to beginning the run. A comparison of the curves in Figures 10 and 9 shows that qualitatively identical results were obtained in the two runs, with respect to changes in the anode and cathode potentials. The addition of iron to the corrosive water resulted in more rapid polarization of the cathodes in Figure 10 than in Figure 9. This effect was especially pronounced in the early hours of the runs. In both runs iron was added continuously to the corrosive waters through the dispersing action of metaphosphate on the corrosion products. Therefore, if the corrosion products in solution enter into the inhibitory action of metaphosphate, the curves for the run to which no iron was added could be expected, in time, to approach those for the run to which iron was added. Comparison of Figures 9 and 10 shows that this actually occurred. On the basis of the curves in Figure 10, it can be concluded that the increased inhibitory action of the metaphosphate in the systems to which iron powder was added (Figure 6), was due to increased polarization of the cathodes in these systems.

Figure 11 has been prepared to facilitate comparison of some of the effects noted in the preceding runs. The 96-hour polarization curves from the runs represented by Figures 7, 8, 9 and 10 have been plotted together in Figure 11. The time of 96 hours was selected

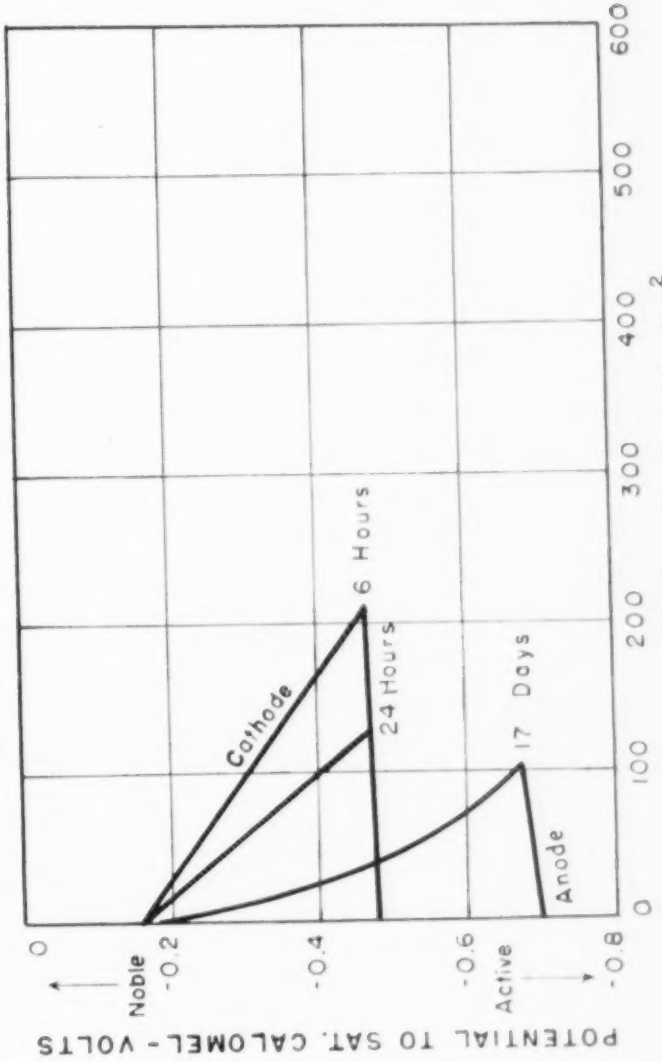

FIG. 10.—POLARIZATION CURVES—50 PPM METAPHOSPHATE—0.5 PPM IRON.

because it was common to all runs. The curves present a reasonably accurate picture of the effects of metaphosphate and corrosion products on the polarization characteristics of the galvanic cells in these runs, as judged by all of the curves in Figures 7-10.

Comparison of curves 1 and 2 in Figure 11 shows that the slight reduction in current flow, with 50 ppm metaphosphate and only one galvanic cell in the system, was caused by a shift of the anode potential in the noble direction. This reduction in current flow was brought about by the metaphosphate in spite of a decrease in the degree of polarization of the cathode. Only a very slight increase in the polarization of the anode can be observed from the increased slope of the anode curve. It is seen from curve 3 that the polarization of the cathode increased with several galvanic cells corroding in the system. Curve 4 shows an even greater increase in cathodic polarization in the system to which iron was added. The increased polarization of the cathodes in curves 3 and 4 resulted in corresponding decreases in the galvanic current flow.

The anode potential in curve 4 is more noble than that in curve 3. This can probably be attributed to a decreased rate of removal of corrosion products in this system by the metaphosphate. In the system to which iron was added (curve 4), some of the metaphosphate combined with the iron, resulting in a decreased affinity of the metaphosphate for iron. It will be noted from Figures 9 and 10 that at the end of 17 days, the anode potentials were almost equal. This indicates that the corrosion products were ultimately removed in the system to which iron had been added. This was substantiated through visual observations. This effect was observed in all of the polarization curves for the systems containing 0.5 ppm iron.

It has been shown that the corrosion products in solution cause a reduction in galvanic current flow in waters treated with metaphosphate (Figure 6). The curves in Figures 7-11 indicate that the reduction in current flow, brought about by increasing amounts of corrosion products in solution, is due to increased polarization of the cathode. In the light of film deposition, current flow, and polarization studies, it can be concluded that the beneficial effect of corrosion products on the inhibitory action of metaphosphate can be attributed to increased deposition of metaphosphate on the cathode, and greater polarization of this electrode.

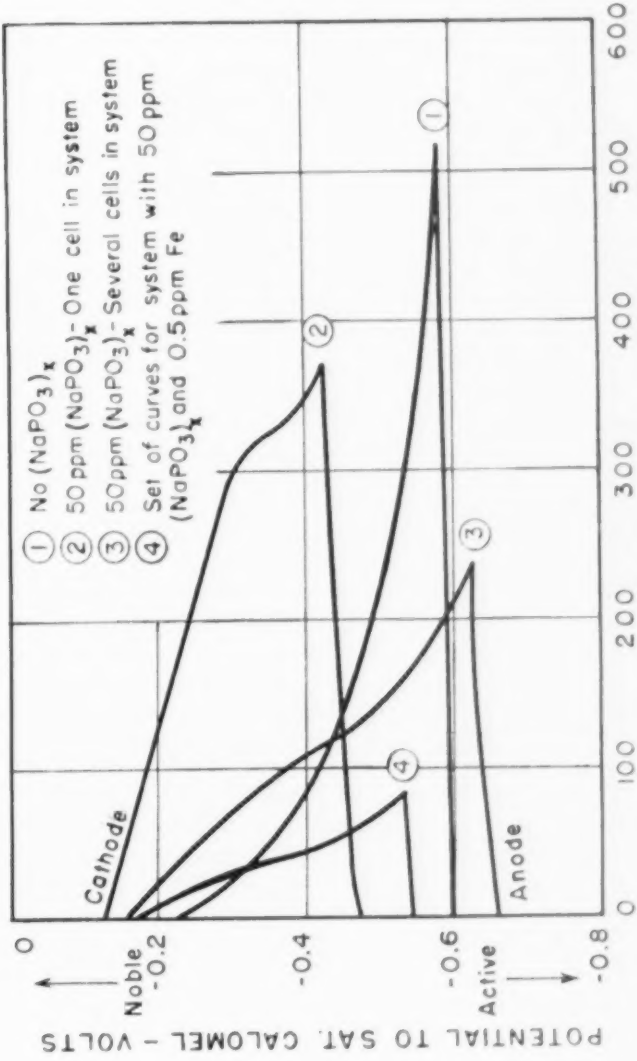

FIG. 11.—POLARIZATION CURVES 96 HOURS FROM BEGINNING OF RUNS.

Single Electrode Potentials

The effects of metaphosphate on the potentials of electrodes in galvanic cells have been discussed in the preceding section. It was the purpose of the research reported in this section of the investigation to find the effect of metaphosphate on the single electrode potential of iron in water.

The equipment and testing conditions used in this experiment were identical with those used in the polarization studies in the preceding section. A single electrode of iron was mounted in the polarization cell. The potential of this electrode was measured against that of the calomel reference cell at the end of desired intervals of time.

The results of this experiment are shown in Figure 12. Qualitatively identical results were obtained in a second run of this type. In the untreated system the potential of the iron changed sharply to a more noble value during the first 24 hours. This was followed by a more gradual potential shift in the noble direction over the remainder of the test period of 17 days. This increased nobility of potential can be attributed to the formation of oxide films on the electrode.

In the system to which 50 ppm of metaphosphate had been added, there was a rapid shift of the potential to a more noble value. This was followed by a decrease in potential, until at the end of 17 days the electrode potential had attained a value comparable to the initial open-circuit potential in the untreated system. At the end of this length of time the potential of the metal in the treated system was far less noble than that in the untreated system. The initial shift of potential in the noble direction can be attributed to the formation of a film of oxides and metaphosphate on the surface of the metal. The subsequent decrease in potential can be attributed to removal of corrosion products from the electrode by metaphosphate, resulting in exposure of a cleaner metal surface. This interpretation of the changes in potential is similar to that presented previously in explaining the changes in anode potentials in the polarization studies. It will be noted that the results obtained in Figure 12, with iron alone, are qualitatively identical with those obtained for the anode potentials and corrosion potentials of the galvanic cells in Figures 7 and 9. Therefore, it is seen that metaphosphate produced results with galvanic cells of steel and stainless steel which were qualitatively similar to those obtained

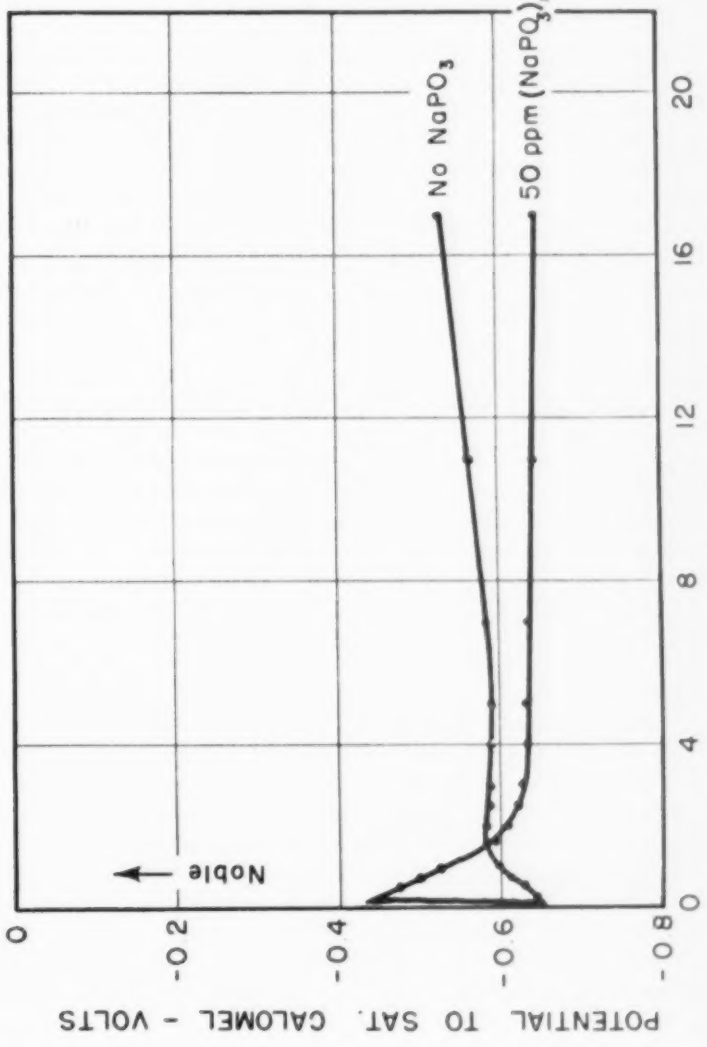

FIG. 12.—SINGLE ELECTRODE POTENTIALS OF IRON IN WATER.

with iron alone. This is in agreement with the findings of Hatch (25, 26).

The effects of anodic and cathodic inhibitors on the corrosion potential have been discussed previously. It can be seen that the initial action of the metaphosphate was similar to that of an anodic or a mixed inhibitor, since its first action was at the anode or at both electrodes of the cell. However, over an extended period of time the inhibitory action changed to that of a cathodic inhibitor, thus tending to confirm the results obtained in the polarization studies. The effects of metaphosphate observed in this study on the single electrode potential of steel are qualitatively similar to those reported by Mansa and Szybalski (23).

Discussion

The results of the studies reported in this paper indicate that the inhibitory action of metaphosphate glass can be attributed to increased polarization of the cathode in metaphosphate-treated water. Although the deposits on the anodes are substantially greater than the deposits on the cathodes, the latter are far more effective in increasing polarization, and therefore in corrosion inhibition.

The results of film deposition and electrical current flow studies have shown that the deposition of metaphosphate on the cathode, and the inhibitory action of the chemical, are enhanced by the presence of corrosion products in solution. Polarization and single electrode potential studies revealed that the beneficial effect of corrosion products was due to increased polarization of the cathode. Further studies have been conducted for the purpose of determining more fully the interrelationship between the effects of metaphosphate and corrosion products on the rate of corrosion of iron in water. The results of these studies have been presented and discussed elsewhere (28, 29), and will only be summarized in this discussion.

It was found that the cathode film contained hydrous ferric oxides, metaphosphate, calcium and possibly other chemicals. The film was formed on the cathode through electrodeposition of positively charged colloidal particles of metaphosphate and iron oxides. It is well known that metaphosphate removes corrosion products from iron. Radioactive tracer studies established that corrosion products entering solu-

tion at the anode were later deposited on the cathode of the corrosion cell. Therefore, the corrosion process can be considered as a source of iron oxides which react with the metaphosphate and are subsequently deposited on the cathode. It was concluded that metaphosphate in solution reacts with corrosion products in the vicinity of the anodes, resulting in the formation of positively charged colloidal particles. These particles, containing iron oxides and metaphosphate, are subsequently deposited on the cathodes through electrodeposition. The film thus formed decreases the rate of corrosion of iron in water by increasing the degree of polarization of the cathodes in the corrosion cells.

It should be pointed out that the findings of this investigation do not negate or conflict with the results obtained by most of the past investigators. In many instances, direct correlation is possible between these findings and those of past investigators. In other cases, the new information brought to light during this investigation may be used to explain conflicting or inconsistent results which have been reported in the literature. A significant example of the application of this new information can be found in the question of whether metaphosphate should be considered as a cathodic, an anodic or a mixed inhibitor.

It has been pointed out that metaphosphate has been classified as an anodic inhibitor (30-32), as a cathodic inhibitor (23-28, 32a, 41) and as a mixed inhibitor (47). No data have been presented to substantiate that this chemical acted as an anodic inhibitor. However, examination of Figures 7 and 8 reveals that under the unusual testing conditions employed for the run of Figure 8, the metaphosphate appeared to act as an anodic inhibitor. In the early hours of the run of Figure 9, the chemical appeared to function as an anodic or as a mixed inhibitor. It can be seen that certan types of short-term tests might lead to the conclusion that the chemical was an anodic or a mixed inhibitor. Longer tests conducted with an insufficient supply of metaphosphate to accomplish stripping of corrosion products, or tests carried out under conditions such that positively charged colloidal particles could not be formed and deposited on the cathode, might lead to the same conclusion.

On the other hand, the testing conditions employed by Hatch (25, 26) for polarization studies included the use of relatively large elec-

trodes in beaker tests. Therefore, the transfer of corrosion products from anode to cathode was facilitated by the proximity of the electrodes. In view of the effect of corrosion products on the inhibitory action, as found in this investigation, it is not surprising that the results of all of these tests showed rapid increases in the degree of cathodic polarization. The erratic data reported by Hatch with respect to anode potentials, are not surprising in the light of the complex action of metaphosphate on anode potentials, as observed in this investigation. The results obtained by Mansa and Szybalski (23, 24), who concluded that metaphosphate glass was a cathodic inhibitor, can be rationalized in a similar fashion.

On the basis of the results of these studies, and the published results of past investigators, it can be concluded that metaphosphate glass is a cathodic inhibitor under conditions normally found in practice. The initial action of the chemical may be similar to that of an anodic inhibitor, due to adsorption of the chemical on corrosion products at the anode. However, it has been well established for many years that with a sufficient supply of inhibitor, the corrosion products are stripped from the metal. Conditions at the anode, where this reaction takes place, are most favorable to the formation of positively charged colloidal particles of iron oxides and metaphosphate. It has been shown that some of the colloidal particles formed in this reaction are subsequently electrodeposited on the cathode and increase the degree of polarization of this electrode (28, 29). Therefore, in the presence of sufficient dosage to produce a metaphosphate residual throughout the system, the corrosion products in the form of tuberculation and rust scale should be removed, and the action of the chemical should become that of a cathodic inhibitor.

It has been pointed out that under normal operating conditions in waterworks practice, corrosion is under cathodic control. Any reduction in the effective cathode areas would result in a corresponding reduction in the over-all rate of corrosion, without intensification of attack.

Therefore, the use of metaphosphate for inhibiting corrosion in a water distribution system would not be expected to lead to excessive tuberculation or to pitting attack in pipelines having low flows, as long as a metaphosphate residual is maintained throughout the system.

Conclusions

As a result of the research described in this paper, the following conclusions may be drawn with respect to the inhibitory action of metaphosphate:

1. The presence of corrosion products in solution increases the inhibitory action of metaphosphate glass.
2. The increased effectiveness of metaphosphate in the presence of corrosion products can be attributed to increased polarization of the cathodes.
3. The initial action of metaphosphate in short-term laboratory tests may be similar to that of an anodic inhibitor or a mixed inhibitor.
4. When properly used in actual pipe lines, where chemical feed is of long duration, the action of metaphosphate would be that of a cathodic inhibitor. Therefore, this chemical should be considered as a cathodic inhibitor under practical conditions.

Acknowledgments

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HOW TO SECURE MAXIMUM BENEFITS WITH ACTIVATED CARBON

BY ALBERT Y. HYNDSHAW*

[*Read January 21, 1954.*]

The average person judges water not by the bacteriological standards, as set up by the State Board of Health, but by those standards which are readily perceptible, i.e., appearance, taste and odor. A water may be sparkling clear, of unquestionable purity, softened to a constantly controlled degree and yet, if a perceptible odor is present, the public confidence which past records have established may be destroyed overnight. Moreover, odorous water often gives rise to a more serious problem, in that the consumer often seeks to replace a safe unpalatable water with a palatable water of questionable purity. Although the water-works operator may be able to explain this odor as a temporary unpleasantry which will have no harmful after-effects upon the community, the memory of this unpalatable water will often remain long after the condition has been corrected. Therefore, it is essential that the water-works operator maintain a palatable water as well as a safe water.

Since the public arbitrarily accepts safe palatable water as a matter of course and becomes highly conscious of an unpalatable water, the water-works operator must avail himself of suitable methods for preventing and/or controlling taste and odors in the water supply.

Activated carbon has proven to be an invaluable aid for correcting taste and odor conditions arising in water supplies. However, the alert and efficient water-works operator, by carefully considering his approach to the taste and odor problem, can obtain the most economical use from his carbon application, as well as the maximum benefits from it.

Prevention

The first approach to any taste and odor problem should be one of prevention.

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For some operators, the problem of preventing tastes and odors narrows to the control of algae growths on the supply. For these operators the following methods are available:

(1) Copper sulfate is used in reservoirs at many water plants to control growths of algae and thereby minimize taste and odor difficulties at the source. Copper sulfate is also used in reservoirs to arrest and destroy algae growths that have attained such proportions as to cause serious taste and odor difficulties.

(2) Activated carbon is used in reservoirs and settling basins for a similar purpose. Carbon excludes sunlight and in this way eliminates algae growths. This treatment is called "Blackout".

However, for many, especially those located in highly industrialized or heavily populated areas, prevention not only involves control over natural growths in the supply as mentioned, but also involves tracing sources of pollution and subsequent attempts to eliminate them. In some instances, the water-works operator will have to exercise some ingenuity for finding the source of pollution. One operator, after exhausting all methods for locating the origin of a phenol pollution, finally located the source by chlorinating samples of water as he went up the river in a boat. The reason that the samples were chlorinated during the tracing was because chlorophenol is noticeable in much lower concentrations than is phenol.

In many cases, preventive measures will go a long way toward reducing the problems of maintaining palatable water. Moreover, the advantages of using these preliminary precautions are often reflected in the subsequent lower operating costs for controlling taste and odor problems when they do arise.

After consideration has been given to the prevention of tastes and odors, the next step should be one of alertness and readiness toward any imminent problem.

Alertness and Readiness

Palatability of water has assumed a position second only to safeness in the water plant, and for this reason methods for detecting tastes and odors have assumed almost the same importance in the

water-works laboratories as that of the chlorine residual test. One of the best methods, and by far the simplest, for detecting and evaluating odor is known as the "Threshold Odor Test".* This test not only provides the operator with a means for checking the odor qualities of the water in his plant, but many times can serve to signal an imminent taste and odor condition. Then, steps can be taken to prevent the tastes and odors from spreading to the distribution system.

The frequency with which the test is used depends upon the character of the water treated; however, the greater frequency of use for it serves to prevent an obnoxious taste and odor from slipping by the attention of the operator. For a supply having a "flashy" stream as its source, it will often be necessary during certain seasons of the year to make odor determinations every one or two hours. In contrast, during normal periods of low odor concentration it may be necessary to run the test only once or twice a day. In many cases where the supplies are taken from a reservoir subject to algae growths, the odor evaluations can often be related to the microscopic examination.

For the average water plant it is suggested that the threshold odor test be run on the raw water and the filtered water: the raw water, because tests at this point will supply the operator with information pertinent to controlling his treatment; the filtered water, because tests at this point will supply him with information as to the effectiveness of his treatment. The data recorded for each test should include water temperature and pH, as well as the characteristics and intensity of the odor, and the current plant treatment. Moreover, the results for these tests should be kept on file for future reference, which will enable the operator to take advantage of a treatment which had provided palatable water for a particular set of conditions in the past, and minimize the preliminary studies necessary to effect a palatable water for the current problem.

Laboratory Study

Laboratory study is the third aspect for the water-works operator to follow, to help him secure the maximum benefits from the application of carbon. When laboratory tests are used to determine the amount of activated carbon necessary to make the water palatable,

*Page 16, 9th Edition, Standard Methods for the Examination of Water and Sewage.

the data may be obtained very easily in the laboratory by following a procedure closely paralleling the jar tests. Before observing the odors, all samples should be filtered through fine glass wool, to remove the carbon. The glass wool should be rinsed with odor-free water and a portion of the treated sample itself, before collecting a sample for the odor evaluation. It is desirable to plot on arithmetic paper adsorption curves for activated carbon, showing the odor concentration as against the applied carbon dosage. With this type of data, the required dosage for any future occurrence of this set of conditions may be obtained by referring to the graph in the file.

At this point it can be noted that adsorption curves on arithmetic paper take a parabolic shape and as the odor concentration increases, the proportionate amount of carbon to be added decreases.

Another point worth noting is that of the relation of laboratory data to plant application. Plant dosages of carbon can often be reduced considerably from that found in the laboratory—in many instances the laboratory dosage has been found to be more than double that required in the plant.

Although we have a method for determining the amount of carbon needed to provide a palatable water, the efficiency of activated carbon is subject to a number of outside influences. Therefore, in order that the water-works operator obtain the maximum utility from the carbon, he must make every effort to recognize these influences and adjust his course accordingly.

This factor suggests the fourth step for the water-works operator to follow in order to obtain maximum usage from his carbon.

Factors Influencing the Application of Carbon

The mechanism by which activated carbon removes tastes and odors is known as adsorption. By this phenomenon, taste and odor bodies are attracted to the surface of carbon and held there. Consequently, the taste and odor bodies are subsequently removed from the water; which action should be contrasted to other taste and odor agents, whose action depends upon changing the chemical structure of the compounds from one form to another.

Since the action of activated carbon is a surface phenomenon, it follows that its efficiency can be influenced by certain conditions com-

mon to water supplies. These conditions can be recognized and, in many cases, controlled by the average water-works operator, as will be shown by the following examples.

Importance of Contact Time

Adsorption by carbon is almost instantaneous and it can be said that the taste and odor bodies are removed from the water as soon as carbon establishes contact with them. However, in the water plant, where the dosage of carbon is generally very small, some contact time must be allowed for the carbon particles to disperse through the system. Therefore, time must be allowed for the carbon to establish contact with the taste and odor bodies. Through experience, we have placed a minimum contact time of five minutes; however, whenever possible it is suggested that 15-minute contact time be provided. In a few isolated instances, *e.g.*, where conditions for pH have been above 10, a satisfactory performance by carbon could be effected by extending the contact time to 30 minutes.

Influence of Hydrogen-Ion Concentration

Hydrogen-ion concentration, particularly for alkaline waters, can have a profound influence upon the adsorption of taste and odor bodies. We ascribe this influence to the formation of a salt—which form of the compound is more difficult to remove by carbon.

Very often the relatively poor efficiency of the carbon can be overcome by increasing the length of contact time. There have been some instances when difficulties arising from conditions for hydrogen-ion concentration have been found in lime softening plants. In most cases, modifying the treatment, so that carbon is applied to the system before the lime is added, will result in a satisfactory performance by carbon.

Influence of Disinfecting Chemicals

As has been mentioned, lime can have a profound influence upon the adsorption by activated carbon. In a similar manner, it can be shown that other chemicals used in the water plant can influence the manner in which carbon behaves, *e.g.*, chemicals used for disinfecting.

Chlorine is universally used for disinfection and in many cases has served to supplement taste- and odor-control methods. The point for applying the disinfecting chemicals requires consideration when

activated carbon is used, in order to obtain the most benefits from both, (1) because chlorine will frequently react with certain organic compounds, producing substances which are more disagreeable to the sense of taste than before treatment; (2) because activated carbon has a tendency to adsorb chlorine and can, under favorable conditions, take up about 10% of its own weight of chlorine.

Therefore, carbon and chlorine should be applied together only when it is impossible to separate the two points of application. This applies particularly when carbon is fed to the top of the filters. When carbon is in suspension (*e.g.*, mixing basin), the adsorption of chlorine by carbon is greatly decreased.

Since there is considerable variation in the manner in which carbon and chlorine can be applied in the plant, examples may best illustrate the several approaches.

The following example, taken from an experience in an Iowa water plant, will serve to illustrate not only the influence of chlorine on the subsequent adsorption by carbon, but also the value of being on guard for any changes in the condition of the water.

During a siege of tastes and odors, heavy prechlorination was practiced, primarily to maintain a chlorine residual in the distribution system. However, this practice intensified the odor in the water so that the amount of carbon needed to be applied subsequently was out of the range of the feeding equipment at the plant. For this particular plant, a palatable water was effected by applying chlorine subsequent to carbon. In contrast, for conditions at another plant it was found that prechlorination, followed by an application of carbon to the top of the filters, effected a palatable water. When this practice was followed, the carbon dosage was cut from 50 ppm to 20 ppm. Moreover, while the application of carbon to the top of the filters shortened the filter runs, the good will gained with the public by maintaining a palatable water more than offset the excess filter washings required.

Effect of Chloramines

The addition of ammonia to the water prior to the addition of chlorine often prevents the formation of malodorous compounds, resulting from the action of chlorine on taste and odor compounds. Moreover unlike chlorine, very little chloramine is adsorbed by car-

bon. The water-works operator frequently takes advantage of this latter factor by using chloramines in plants where chlorine has been found to accentuate and set the odors—or in plants where it is necessary to apply carbon and the chemical for disinfection in close proximity.

A city in Louisiana can be used as an illustration. This city practiced free residual chlorination (2-3 ppm free chlorine was used to remove from the water the woody odor present). Not only was this application ineffective for reducing this type of odor in the water, but subsequent observations showed that the odor was accentuated; and consequently, very large dosages of active carbon were necessary to effect a palatable water. Subsequent work showed that a palatable water could be obtained by changing to a chloramine treatment, followed by an application of carbon.

Influence of Disinfecting Chemicals Other than Chlorine

Other chemicals, such as ozone and chlorine dioxide, have been used for disinfecting purposes. However, to date, their use has been limited and data concerning interference with carbon has not been available. If these chemicals are to be used for disinfecting in the future, we may expect that they will influence the selection of the point for applying carbon, just as has been found when chlorine is used.

Year-Round Application of Carbon

Some operators consider a fifth aspect necessary in order to obtain maximum utility from carbon application, *i.e.*, year-round feeding of carbon, even though in some cases only a fraction of ppm may be involved. These operators report the following benefits derived from the year-round application of carbon:

(1) The application of carbon to stabilize the sludge has been reported to have distinct advantages over chlorine. Carbon not only does a better job of sludge stabilization, but, in so doing, allows the operator to operate the settling basin over a longer period of time without cleaning. Moreover, with this continuous application of a small amount of carbon, the

sludge is conditioned so that it is easier to remove during the cleaning operation. One operator reports that this latter factor in itself is a distinct advantage as a labor saver.

(2) Another advantage, offered by the year-round use of carbon, which is frequently neglected is that of better floc formation, and in a number of instances this has resulted in the use of less alum. Carbon, when applied for this purpose, is reported to be more efficient when applied in very small dosages (less than 1 ppm) than much larger dosages. In this connection, it may be well to mention the problem of carbon passing through the filters. When carbon comes through the filters, it is a sign that the filters are not removing all the materials they should. Carbon is serving as an indicator and its presence suggests that other materials are passing through the filters. Correction of this difficulty does not involve eliminating the carbon, but involves adjusting the floc formation so as to form a better floc. Frequently, this can be accomplished by adding a very small amount of carbon along with the alum solution, so as to promote better flocculation and settling.

(3) The third advantage offered by the year-round application of carbon arises from the fact that carbon will attract to its surfaces foreign compounds, not necessarily taste and odor bodies, and subsequently remove them from the water. A comparison of the quantity of organic material remaining in the treated water was made in a study at a plant which had practiced free residual chlorination for some time. These data showed that water not having a carbon treatment contained 105 ppb. organic material, whereas water treated with carbon had 37 ppb. (a reduction of approximately 65%).

Summary

To summarize, the water-works operator may obtain the maximum benefits from his application of activated carbon by giving consideration to the following aspects:

(1) Whenever possible, he should take steps to prevent any formation of taste and odor conditions in the raw-water supplies.

(2) The water-works operator should be alert and ready for any imminent taste and odor condition.

(3) When available, the laboratory should be used to supplement any plant treatment. Often, well-kept laboratory data will eliminate a great deal of preliminary study for a taste and odor condition.

(4) Every water-works operator should recognize that the manner in which carbon is applied will vary according to the individual plant. Therefore, he should determine for his plant the most effective point for applying carbon.

(5) He should be aware of the benefits derived from the year-round application of carbon, which some operators have reported to effect a more efficient operation of the water plant.

CHLORINATION—THEORY VERSUS PRACTICE

BY V. W. LANGWORTHY*

[*Read at Chemists' Round Table, Feb. 18, 1954.*]

An interesting observation has been recorded that "in water purification, as in the somewhat allied field of sewage purification, there is a tendency to follow blindly in the wake of authority or novelty, forgetful that no two problems are the same and a treatment which may be excellently suited for one case is out of place in another." Dr. Gilbert J. Fowler included these words in a paper published in India in 1923 (1). He was correct then and the thought applies in many cases today.

It is safe to state that water chlorination has moved out of the novelty class and authority implies that it is here to stay, until a superior replacement comes along. Chlorine became commercially available in 1909, but was not accepted blindly as a water-purification chemical. Court action and legal decisions were required to establish water chlorination as a process beneficial to the public interest. Mankind resisted a change even when evidence was at hand that typhoid fever could be controlled through effective public health measures.

Chlorination was and still is a means of disinfecting water intended to be made potable, though other applications have evolved through four decades of experience. Those of us who are concerned with water treatment are aware of instances where theories do not always apply directly to practice. We are also aware of instances where theory has received insufficient consideration to be proved in actual practice. It is the purpose of this discussion to provide examples of these situations.

Prechlorination

When chlorine is added to a water prior to any other treatment, disinfection and other objectives may be sought. It is in attainment of other objectives where subtle acceptance of authority or novelty

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is likely to occur. Chlorine, added to a raw surface water in amounts sufficient to satisfy the chlorine demand, will not exert bactericidal results with consistency and such marginal chlorination may contribute to tastes and odors in the finished water. Chlorine is a disinfectant then, but it may also produce disagreeable results when proper control is lacking.

Free ammonia was found to have a strong influence on chlorine demand and studies showed that residuals composed of chlorine and ammonia provided disinfection without producing tastes and odors. Theory indicates that a chlorine to ammonia ratio of 1 to 3 should provide a slight excess of ammonia. The facts are that ratios as high as 1 to 12 may be required to accomplish the objective. Combined chlorination is extensively practiced, however, with eminently successful results. Each case must be taken on its own merit, regardless of what combination works elsewhere.

Breakpoint and superchlorination similarly must be applied as local conditions dictate. A working example of this may be found in Adrian, Mich. Additions to the water-filter plant were designed to increase capacity and include provisions for lime-soda softening. Free residual pre-chlorination had been practiced from the first day the filter plant was placed on the line. Aluminum sulfate was the coagulant and two-hour retention was provided prior to rapid sand filtration. These were excellent conditions for breakpoint chlorination, which was necessary to provide taste-free water in the distribution system. The raw water contains no industrial wastes, but decaying vegetation and other materials proved susceptible to 2.0 ppm free residual chlorine in the two hours contact provided.

Contrast this experience with design conditions of the plant addition which provided eight minutes contact between the raw water and chlorine. Plant improvements in 1950 included lime-soda softening, which means that a pH of 10.5 or 11.0 had to be reached immediately after the eight minutes' chlorine contact time. This situation is inconsistent with the theory that less free chlorine activity is exhibited at high than at low pH. Of course, some germicidal effect is realized from the high pH necessary for the softening reaction. Design should have included provision for more contact time following pre-chlorination. There is a happy ending, because tastes that are not removed by

pre-chlorination are now effectively handled at the filter influent with chlorine dioxide.

At Ann Arbor, Mich., advantage is taken of thirty minutes' contact time in the raw-water transmission line. Pre-chlorination effectively removes tastes and odors before softening doses of lime are applied.

The lesson to be learned is that plant design should be based on theory *and* experience, if possible. It must also be realized that chlorine dioxide worked, fortunately, at Adrian and that thirty minutes' contact time at Ann Arbor applies to raw water received there. Difficult taste and odor problems may require super-chlorination with dechlorination after periods of extended contact, to provide a normal residual in the finished water.

Postchlorination

Taste and odor must manifestly be controlled at the treatment plant. Postchlorination, or plain chlorination, is practiced for disinfection and to provide an effective chlorine residual in the distribution system. Free residual or combined residual chlorination may be selected, depending on local conditions. It may be of interest to examine these residuals as they apply to the finished water.

Butterfield (2) and his coworkers studied free and combined chlorine to determine their relative germicidal efficiencies. It is of interest that their studies show 25 times more chloramine than free chlorine is required to obtain complete kill in the same contact time. They also report that chloramine requires 100 times longer contact time as free chlorine to obtain complete kill using equivalent dosages.

It would appear that these studies should have a bearing on the decision to carry free or combined chlorine in the water mains. In practice, we often find it difficult to maintain a free chlorine residual to the ends of the distribution system. Organic materials within the piping may produce disagreeable tastes when subjected to water containing free chlorine.

Williams (3) has investigated the problem of de-chlorination in the distribution system at Brantford, Ontario. His experiments suggest that ferrous iron acts as a dechlorinant and destroys chloramine residuals. The presence of ferrous iron in trace amounts could be

caused by corrosive water and could feasibly be controlled by close attention to producing a balanced water. We attempt to provide a chlorine residual which will persist throughout the water system. As Williams writes, "the maintenance of residuals of increased stability would best eliminate biological forms from distribution systems". An important factor to be remembered is that a "stable" residual is also a less active residual, as Butterfield showed.

We often find ourselves in a dilemma, because free chlorine residuals are effective, yet it is impossible to maintain them to all points on the system. If we establish combined chlorine residuals, they may persist, but how effective are they? Butterfield was working with enteric pathogens and coliform organisms, which we must keep from the consumer at all costs. One method by which this may be accomplished is to disinfect completely at the treatment plant or pumping station, and work on the distribution-system problems separately. The presence of biological life would indicate the necessity of proceeding in some manner to destroy it. Anaerobic life could be discouraged by maintaining dissolved oxygen in the water. Adjustment of pH to obtion maximum benefit from chlorination is possible, provided corrosion is not stimulated.

A long-term procedure has been reported by Wilson (4) which consists of removing a water main from service between midnight and morning. Chlorine dosage of 50 ppm is allowed to stand for two hours in the main, followed by a thorough flushing. This procedure at San Diego has made it possible to carry high chlorine residuals throughout the system. A similar, but less desirable, procedure has been reported by Goudey (5), where free chlorine residuals are established at the plant. A progressive cleaning process is instituted, the progress of which is encouraged by systematic flushing. Determinations for iron are made until no iron pickup is noted throughout the system. It is suggested that the method described by Wilson would cause less difficulty with consumers.

It is possible that intermittent chlorine dosages would alleviate the biological problem in the piping system. The San Diego Aqueduct now receives intermittent chlorination, which is effective in slime control, where a constant rate permitted the organisms to grow and restrict water flow. We could conceivably increase chlorine dosage inter-

mittently above normal levels and accomplish the same objective in a distribution system.

We have much to learn about conditions inside the walls of the piping system. The effects of corrosion are well known, for example, but the ideal method for eliminating it has yet to be found. Routine bacteriological sampling gives confidence that the consumer is getting safe water, but no guidance as to biology within the water system is provided.

Dosage Control

It is important that desired objectives of chlorination be fully understood by each person responsible for treatment control. At a minimum, chlorine dosage must be continuous and of sufficient magnitude to do the work required. Bacteria are not aware that chlorine is supposed to kill them. Tastes and odors will not automatically succumb to chlorination. Chlorine is not a cure-all for every water-supply ailment, but where it is specific, proper dosages must be accompanied by intelligent control.

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THE WEST BOYLSTON WATER DISTRICT WATER SYSTEM

BY LOUIS C. CAMPBELL*

[Read February 18, 1954.]

West Boylston is strictly a residential community, situated six miles north of Worcester, the Heart of the Commonwealth. The population is approximately 2,900.

In the early 1890's, when the Metropolitan Water Supply Committee was looking around for more water for the city of Boston, it was decided that the valley between the Quinapoxet and Stillwater Rivers was a very likely place for a reservoir. At this time the town of West Boylston was a thriving mill town with a population of 3,000. The Commonwealth bought the property along the shores of these rivers, moved some of the houses out of the valley, and in 1895 proceeded to make a reservoir, later to be known as Wachusett Reservoir, taking the water from this watershed for Metropolitan Boston. The land taken for this reservoir included 1,127 acres of West Boylston, the greater part of which is now under water.

At the annual Town Meeting in March, 1892, a Committee had been appointed to study the possibility of establishing a water system for the town. An engineering survey was made by the firm of Shedd & Sarle, but at this time the town was not ready to go into such a project, evidently not believing that the State would take this valley for a water supply.

After the State had started work on the reservoir, the mill-hands moved to other communities to seek a livelihood, and the population decreased steadily for the next twenty years. The high population of 3,000 in 1890 dropped to a low in 1910 of 1,270.

In 1916 there was a movement among certain townspeople toward obtaining a town water system, as it was thought at that time that all the water from this watershed was being diverted into Wachusett Reservoir and lowering the water table in the town, thus affecting the wells. Another committee was appointed to look into the matter,

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and William S. Johnson, Civil Engineer of Boston, was engaged to make a survey. He made a very exhaustive study of conditions and his report was presented to the town, but still the town was not ready for a water system.

From 1910 on, more people had come to make West Boylston their home and by 1933, when the town tried for a third time to get a water system, the population had increased to approximately 2,100. In this year, a bill was introduced into the Legislature, later known as Chapter 352 of the Acts of 1933, which, if passed and accepted by the town, would give it authority to establish the West Boylston Water District of West Boylston. The bill was passed by both branches of the Legislature and signed by the Governor, and became a law July 22, 1933. The time limit for the town to accept this Act was set at four years after its passage.

The years passed and no action was taken by the town to form a water district. This was not the end of hope for the water district, however, and on March 11, 1939, Chapter 55 of the Acts of 1939 was passed, amending the original Act of 1933, and extending the time of accepting Chapter 352 to eight years.

At the annual Town Meeting February 6, 1939, a Committee of 25 was appointed and authorized to engage a competent hydraulic engineer to make a survey, including plans and estimate of costs, and to report back to the town on or before May 31st, 1939.

The report was made on May 27th, 1939, and the Committee was authorized to investigate further. They consulted with various engineers and finally agreed that Whitman & Howard's Report was the most complete, and that they should go along with this report and call a meeting to have the town accept Chapter 352 and establish a water district. The special meeting was called on November 8th, 1939, and the town voted to accept the Act and form the West Boylston Water District of West Boylston. Three Water Commissioners were elected at this meeting.

In 1939 Paul Howard visited West Boylston, to look around for a suitable well site, and investigated the possibilities of taking water from the Wachusett Reservoir. With the permission of the Metropolitan District Commission, Whitman & Howard had two test wells driven along the shores of the Wachusett Reservoir, one 44 ft deep and

the other 22 ft deep, but in neither well was there suitable water-bearing material from which the District might obtain a water supply.

The location finally agreed upon by Mr. Howard and the Committee was a gravel pit, situated about two miles from Wachusett Reservoir. A test was made here and the water table was only one foot below the surface of the ground. The necessary pumping test was made for quantity and quality, and the State Department of Public Health gave its approval of this supply.

It is interesting to note why we did not take water from the Wachusetts Reservoir. A paragraph from the report of William S. Johnson, civil engineer, made in 1917, reads as follows:

"Perhaps the most natural place in which to look for a water supply is the Wachusetts Reservoir of the Metropolitan Water Works, the upper end of which is almost the center of the portion of the town to be supplied with water. The Legislature has provided that the town should have the right to take water from this source for water-supply purposes.

"There are, however, several serious objections to the use of this water. The water at this end of the Reservoir just below the entrance of the Stillwater and Quinapoxet Rivers is highly colored, and, at times of high flow of the rivers, is turbid and otherwise of objectionable quality. A supply from the Wachusett Reservoir would not be perfectly satisfactory and the cost of obtaining the supply,taking into consideration the difficulty in pumping from different depths, is likely to be as great or greater than the cost of a supply from wells. We do not recommend the use of the Reservoir."

The Report made by Whitman & Howard in 1939—22 years later—reads as follows:

"You have a reservoir in your town, the Wachusett Reservoir, which has served as a principal water supply for the Boston Metropolitan District for many years, from which you may take up to two million gallons per day. However, since West Boylston is located at the upper end of the Wachusett Reservoir, the water would be highly colored at times and might contain objectionable bacteria, as the water would not receive the benefits derived from a long period of storage; but a water supply might well be taken from this reservoir at this location, if filtered. Since there is no other reservoir or suitable location for a reservoir, and since West Boylston is located at the upper end of the Wachusett Reservoir, we do not recommend obtaining a water supply in this manner, if a good ground supply can be found."

In 1940 the Board of Water Commissioners had their work cut out for them. This water-works business was a new field for them.

They agreed to accept the recommendation of the Survey Committee and engaged Whitman & Howard as engineers to install our system. The Board visited neighboring districts to get what information they could. They interviewed representatives of all branches of the industry, and took time from their busy lives to visit the Johns-Manville factory in New Jersey, to get first-hand information on the manufacture of transite pipe. They were accompanied by a representative from the engineers.

Then came the application to the Federal Government for financial assistance through the W.P.A. This approval to our request was granted and we were allotted $350,000. The treasurer of the District was authorized to borrow $135,000 for a period of 30 years, which really put the District in the water-works business.

Contracts were let to R. E. Chapman Co., of Oakdale, Mass., for two gravel-packed wells, and on July 15th, 1941, the W.P.A. started work with 100 men. The W.P.A. manpower varied from 100 to 500 during the course of construction.

Our first two wells were put down in the same location, approximately 150 ft apart, to a depth of 45 ft, and we found all the water we needed. They are both eight-inch wells, with a Fairbanks-Morse pump capable of pumping 150 gpm—one station having a stand-by gasoline engine for emergency purposes. The water is pumped directly into the system; no chlorine or other chemicals are added, and the water never sees daylight until it comes out of the faucet in the homes.

Our reservoir was being built while trenches were being dug, and the work was progressing according to plans. Our reservoir is of the groined-arch construction type, 72 ft by 88 ft by 9 ft, and holds 460,000 gal. of water. It is built of concrete on solid ledge, at an elevation of 794 ft above sea level. The pumping-station elevation is 644 ft above sea level. The elevation at the center of the town is 494 ft, so that we actually have a 300-ft elevation over the town. With this 300-ft elevation for our reservoir, it was necessary to install two pressure-reducing valves on the main lines out of the reservoir in different sections of the town. These are set at an elevation of 535 ft and reduce the pressure by 50% before it comes into the town.

By the Fall of 1942 the W.P.A. was about to close down and our system was not fully completed. The Board of Water Commissioners

had received assurance from the W.P.A. Coordinator that he would work along with them as long as possible. The Commissioners had different ideas as to what was most important to do to make a complete system. One Commissioner insisted that both sides of the reservoir should be connected to the system, as planned by the engineers, regardless of what had to be sacrified in the way of mains in the streets. Both the engineers and the W.P.A. Coordinator went along with the idea and, thanks to this one Commissioner's insistence, both sides of our reservoir were connected to the system before the W.P.A. closed down on December 31st, 1942. Thus the District could be supplied independently from either side of the reservoir, in case of a serious break in the mains.

We had installed 13 miles of pipe, set 90 hydrants, and had 68 house services the first year of operation. Our first house connection was made October 12th, 1942. On the advice of our engineers, we use nothing but cement-lined wrought-iron pipe for house connections. Every year since the start of operations the District has been faced with putting in extensions, and the District has grown beyond any estimates given us by our engineers.

In 1950 the Board of Water Commissioners requested the engineers to make further studies of our system and such recommendations as they thought necessary, keeping in mind the growth of the District. They were also requested to find another location for a supply of water for the north side of the town. The town is divided practically into two sections by the Wachusett Reservoir. The engineers made quite an extensive report and the Board went along with their recommendations, which required a special act of the Legislature to allow the District to borrow money to do the work as recommended.

We installed a high-pressure line in one area where the pressure was very low, increasing the pressure by 60 lb. We still have another installation to make in a low-pressure area.

We installed two surge-relief valves in two sections of the District, to relieve the pressure on the north side of the town, where it has a tendency to build up.

Early in the year we changed the recording device at the reservoir. We installed a liquid-level control, which tells us at a glance the height of water in the reservoir. A pressure-drop alarm was installed

at the home of the superintendent, which records any excessive drop in pressure.

We have installed a new well in the same field where our other two are located. This is a ten-inch well and has a Fairbanks-Morse pump, capable of pumping 300 gpm. This pump kept us well supplied during the four-month dry spell in 1953. The water in this well never dropped lower than 3 ft 6 in. below normal.

In the Summer of 1953 another well was driven in the north side of town. The Board was very anxious to get a supply on this side of Wachusett Reservoir. According to the water pumped, we are told it is good for 1 mgd. It has not been developed yet, but will be done this coming Summer. A reservoir or standpipe of some sort is contemplated in this same general location. With these four wells, the engineers feel we are well taken care of for some time.

It is interesting to compare the report may by Johnson in 1917 with that made by Whitman & Howard in 1939, as to the location of standpipes or reservoirs, sizes of pipes, and pressure-reducing valves. Twenty-five years did not change the report much. It was estimated we would use 300,000 gal per day and we should provide for same. We are pumping approximately 250,000 gal per day. In 1953 we pumped a total of 71,187,595 gal.

In new developments, the developer is required to furnish all material, except hydrants, do all the necessary work, and then give the District a quitclaim deed for same, which must be recorded with the Registry of Deeds. Size of pipe, location, etc., are decided by the Board of Water Commissioners after the plan of the development has been approved by the planning board. At the present time we have four such developments under way, with approximately 175 houses to be built.

A few facts about the District follow:

As of January 1st, 1954, we have approximately 29 miles of pipe, 170 hydrants and 749 water takers. The engineers estimated 300 at the end of ten years. Fifteen years ago nobody would have estimated that West Boylston would grow so fast.

The system is 100% metered.

The system is 100% class 150 transite pipe—6″, 8″ and 10″ sizes.

We do not have a hydrant tax, but a water tax based on the real estate valuation. The tax rate in 1941 was $1.44 per thousand valuation. In 1933 it was $10.00 per thousand valuation.

The valuation of the District in 1940 was $2,136,520 and in 1953 it had increased to $3,690,180.

Our population has increased from 1,822 in 1940 to approximately 2,900 in 1953.

The Board of Water Commissioners is very insistent that money due the District shall be paid when due, with the result that on January 1st, 1954, not one cent was owed the District for water consumption.

Total billings for water consumption for the year 1953 amounted to $22,499.38.

Water District tax billings for the same period amounted to $36,901.80 and as of January, 1954, there was only $1,205.21 outstanding.

The Board of Water Commissioners has done a good job and is to be congratulated, and West Boylston has a water system of which the citizens can be proud.

DETERMINATION OF CHARGES FOR PUBLIC FIRE PROTECTION

BY DARRELL A. ROOT* AND THOMAS R. CAMP*

[*Read October 6, 1954.*]

INTRODUCTION

The primary requirement of a water-works system is that it have the capacity to perform its two principal functions: the supply of water for general consumption and the supply of water for fire protection. It is from the performance of these two functions that a water works usually secures its revenue in the form of charges for the water consumed and charges for the fire-protection service afforded. It is obvious that the most equitable method for distributing charges is for the consumer to pay for the actual water used for general consumption and for the property protected to pay in addition for fire protection. The difficulty, however, lies in determining what is an equitable distribution of charges.

During the many years in which the subject of fire-protection rates has been discussed, we believe there has been general agreement in the principle that each function of the water-works system should pay for the cost of providing that function. With this in mind, the various items of expense in the water-works budget, such as hydrants, meters, services, etc., can be assigned to the function for which the item is used. For example, hydrants, including their connections and gates, should be assigned to fire-protection charges; services, meters, small distribution mains, and purification works should be assigned to the functions of general consumption. Any other special service, such as private fire protection, should be charged to that service.

The allocation of the cost of the remaining parts of the assets of the water works which are used jointly by fire protection and general consumption can be made by the following general methods:

(1) public fire protection as an incremental cost,
(2) general service as an incremental cost, and
(3) the capacity-ratio method.

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The "capacity-ratio method" assumes that fire protection is of no less importance then general service and provides for the allocation of costs of a joint nature on the basis of some relation between the capacity required for public fire protection and the capacity required for general service. One division of the joint cost is made on the ratio of the cost of a hypothetical system for fire protection only to the cost of that system plus the cost of a hypothetical system for general service only.

The "general service as an incremental cost" method assumes that fire protection is the primary function of the water-supply system and that only those charges not utilized by fire protection should be made to general service.

"Public fire protection as an incremental cost" is the converse of the latter method and assumes that public fire protection should be charged with only the incremental cost above the cost required for a general service plant.

Our firm is of the decided opinion that the function of a water-supply system is first to provide a safe and adequate supply of water for general consumption and that fire protection is an added benefit supplied by the water-works system. On the basis of this premise it follows quite naturally that we believe the most equitable means of assessing fire-protection charges is the method of "public fire protection as an incremental cost."

Previous Studies of Reasonable Return for Fire-Protection Service

The first paper on fire-protection rates published by the A.W.W.A. was by F. L. Fuller in 1888. Since that time many articles and discussions have been published by the A.W.W.A. and other organizations. In order to bring some of the previous thinking more clearly into focus, we have summarized what we believe to be the most important ideas on the subject and present them herewith.

Metcalf, Kuichling and Hawley

In 1911, Leonard Metcalf, Emil Kuichling and William C. Hawley presented the results of a most significant study—"Some Fundamental Considerations in the Determination of a Reasonable Return for Public Fire Hydrant Service"—published in the Proceedings of the

American Water Works Association, 1911. This study outlined a method for calculating the income which should be obtained for public fire-protection service, and was based on the belief that charges for fire protection should at least equal the cost thereof. In general, their proposed method for prorating costs between the service of furnishing water for general consumption and the service of supplying water for fire protection was derived from a comparison of the capacities of the facilities required.

The expense of fire-protection service bears no relation to the amount of water used, for while a large part of the water plant is held in readiness for the purpose of fire protection, the use of water for this purpose is relatively small. Metcalf, Kuichling and Hawley reasoned that the best way of allocating charges between consumption and fire protection was on the basis of the capacities required for each service. Finally, it was their opinion that the function of a water plant is first to supply the needs of general consumption and secondly to provide fire protection; therefore, the determination of the cost of fire protection should be based on the cost of the incremental or additional capacity required in the water system for fire protection.

The results presented in this paper were in the form of several diagrams and curves, based on data obtainable at that time. An empirical formula was presented to represent the authors' best opinion of that portion of the fixed capital investments chargeable to fire protection. The authors were aware of some of the limitations of their formula and called attention to the fact that their studies were of comparative value only as indicating general tendencies and that in any individual case they would expect substantial departure from the normal conditions which they assumed. Their assumption that the cost of a distribution system is proportional to the capacity is in error, and there is no evidence in their paper that they were aware of having made this error.

The Metcalf, Kuichling and Hawley formula is:

$$Y = \frac{147}{X^{0.31}} - 12.1$$

where Y = the percent of the total fixed capital chargeable to fire protection

and X = the population served by the system in thousands.

If this equation is applied, the results will be much too high, because it is based on the erroneous assumption that pipeline cost is directly proportional to flow capacity. The magnitude of this error will be demonstrated later in this paper.

Manual of Water Works Practice, American Water Works Association, 1929

The Water Works Practice Manual of 1929 went into considerable detail in outlining a method for determining reasonable charges for fire-protection service provided by public water supplies. The fundamental basis of this method was that the charge should equal the cost of the service. In applying the method it was assumed that the first cost of a distribution system is proportional to flow capacity. The proportional cost of fire-protection capacity is taken as the ratio between the required fire flows and the sum of the required fire flows and maximum daily demand.

In outlining the proposed method, no assumptions were made as to the water consumption that could be expected for any average water-works system. For determining the required fire flows the Manual recommended the National Board of Fire Underwriters' Standards or other standards which appear most reasonable for the case under consideration. In the determination of the charges for fire-protection service due to fixed costs, depreciation, taxes, maintenance and repair, the Manual recommended that the capacity ratio be applied directly to these expenses in those portions of the water-works system which are used jointly for the supply of water for general consumption and for fire protection. The expenses of the portions of the system which are not used jointly, such as the hydrants used only for fire-protection purposes and the very small distribution piping, which has no value in fire protection, should be charged directly to that service to which they belong.

Joint Report of Committees of the American Society of Civil Engineers and the Section of Municipal Law of the American Bar Association, 1951

"Fundamental Considerations in Rates and Rate Structures for Water and Sewage Works", a Joint Report of Committees of the

American Society of Civil Engineers and of the Section of Municipal Law of the American Bar Association, 1951, contains a discussion of the problems of allocation of costs of public fire protection. The Committee's approach to the fundamentals involved in the problem of determining basic rates for public fire-protection service was based on the following considerations: first, the rates charged for fire protection should be equal to the cost of that service; second, the quantity of water used does not represent a fair basis for the allocation of fire-protection costs; third, a major element in the cost of water is created by the necessity of being ready to serve and these costs do not vary with the quantity of water actually used; and fourth, the most equitable method by which the cost of fire-protection service can be determined is by the "Capacity-Ratio" Method. In the Capacity-Ratio Method the allocation of all costs of a joint nature is made on the basis of the ratio between the capacity required for fire protection only and the capacity required for fire protection only plus the capacity required for general service.

In discussing the various possible methods by which the cost of fire-protection service could be determined, the Committee states that first there should be a direct assignment of certain items which are used for one purpose or another and not jointly for fire protection and general consumption. Special fire mains, fire hydrants and appurtenant structures should be assigned directly to the cost of fire protection. Meters, services, purification works and small distribution mains are assigned mainly to the cost of functions other than public fire protection.

The method preferred by the Joint Group is the Capacity-Ratio Method, which is based on the opinion that neither general service nor fire protection is more important than the other. One approach to the determination of relative capacity involves estimation of the cost of two systems. One system would provide only fire protection and the other would provide only the works required for general consumption. The relative charge to fire protection can then be determined as the ratio of the cost of the system for fire protection only to the sum of the cost of the fire-protection system and the cost of the system for general service only.

The Joint Group believed that a less cumbersome and more flex-

ible basis for application of the Capacity-Ratio principle involves the use of flow capacities in the ratio instead of the costs of the systems. Since the Joint Group believed that this method is the most fair and reasonable means of allocating the joint costs, it is dealt with in some detail in their report.

A.W.W.A. Committee Report—Louis E. Ayres, Chairman

The report of the Committee on Determination of Water-Rate Schedules was published in the March, 1954, issue of the American Water Works Association Journal and states in part:

". . . Although most water works managers and engineers have generally accepted the propriety of charging for public fire protection, and courts and commissions have usually included allowances for this service in rate structures, such a charge is lacking in most municipally-controlled water works. Privately-owned properties usually charge for fire protection, but frequently in nominal amounts.

"Among the factors that have contributed to this state of affairs are: (1) a general feeling that the theories of computing the fire charge have overemphasized the cost of this service; and (2) the fact that a fire charge has been an additional item in a tax budget which is already inadequate for other municipal needs. Under such circumstances, if one hopes to effect any improvement in a confused situation, a more realistic approach is required, both in the method of computing the fire charge and in the manner of its collection.

"In computing the charge, one should accept the premise that the prime function of the average municipal water works today is to supply a commodity, and that fire protection, although important to the safety of the community, is a supplementary service, the charge for which should not exceed the demonstrable additional costs involved in rendering this service.

"The direct additional costs include: (1) the fixed and operating charges arising out of all plant and equipment installed solely for fire protection, such as hydrants and their connections, and any pumps, mains, storage, or other equipment used only for fire service; and (2) the cost, at normal commodity rates, of the water used in fighting fires.

"The determination of indirect costs—those costs that arise out of the additional plant capacity required for fire protection—has been a difficult hurdle in the past. The mechanics of this determination, particularly as applied to distribution facilities, have been complicated even more by the improved definition of fire demands. . . .

". . . The additional cost of distribution facilities may account for much of the cost of fire protection. An accurate determination would require cost estimates based on two systems—one for fire only and a second capable of

meeting the combined demands of fire and general service. Although such estimates could be made by commissions and larger cities, with the aid of rate specialists, it appears that most determinations have been made without such analyses. . . ."

This report also presents an alternative approach to the fire-protection charge, involving the assumption that storage may be provided in lieu of capacity, and a method is presented on the basis of this assumption.

Discussion of Previous Studies

Perhaps the most noteworthy feature of the Metcalf, Kuichling and Hawley paper is the fundamental idea on which the authors base their reasoning, that is, that the charge for fire protection should be an incremental or extra charge above that of supplying water for general consumption. It was not questioned to the best of our knowledge in the wide discussion which followed the presentation of the paper. This concept appears to have been adopted by the Water Works Industry, Public Utility Commissions and Underwriters, and was not questioned until much later.

The fundamental ideas represented by the recommendations in the Manual of Water Works Practice are as follows: that the charges for fire-protection service should be equal or related to the cost thereof; that for any water-works system, construction cost is directly proportional to capacity; and that the allocation of cost between the two services, that is, fire protection and general consumption, should be in proportion to the ratio of the flows required for each service. It should be noted as well that the Manual made no effort to formulate the cost of fire-protection service for an average water-works system but instead recommended the procedures to follow, using the data which are usually available for most water-supply systems.

Of the basic considerations brought forth in the report of the Joint Committee there are several which should be noted in particular. The opinion of the Joint Group that the consideration of the cost of fire-protection as an incremental cost is not a fair and equitable practice hardly seems justified. Much of the difficulty in obtaining equitable rates for fire-protection service originated in the negotiations leading to the establishment of water-works companies. The demand for water service was so strong that seldom was any effort made by

the consumers to see that a just charge for fire-protection service was distributed among the taxpaying population. As a result, many charges for fire-protection service are much less than the cost of furnishing that service. The older water-works systems of this country were established for the primary purpose of furnishing water for general consumption. Thus, it would seem that the most equitable method of considering the cost of fire protection would be by assuming that such costs are incremental.

An analysis of the three methods described by the Joint Group, *i.e.* "General Service as an Incremental Cost", "Public Fire Protection as an Incremental Cost" and the "Capacity-Ratio Method", shows that there will be no differences in the share of the undivided fixed assets chargeable to fire protection if the same flows are used for all three methods and costs are assumed to be in proportion to capacity, as was done by Metcalf, Kuichling and Hawley and also by the Joint Group in its development of the "Capacity-Ratio Method". If, however, costs are not assumed to be proportional to capacity and are actually estimated for the alternate systems for each method, it will be found that the first method, (*i.e.* "General Service as an Incremental Cost") gives the highest cost for fire protection and the second method (*i.e.* "Public Fire Protection as an Incremental Cost") the least cost. This is a very important conclusion which appears not to have been recognized before and it probably has accounted for much of the confusion in thinking about equitable charges for fire protection.

At this point it becomes necessary to demonstrate that the cost of distribution pipes is not proportional to their capacity and that substantial errors result if cost is assumed proportional to capacity. The actual total cost of distribution mains per foot of length constructed during 1950-'52 in a large New England distribution system has been plotted in Fig. 1 against capacity for hydraulic slopes of 1 and 10 ft per 1,000 ft. It will be noted that the actual cost varies at a considerably less rate than direct proportionality. For example, to double the capacity of a 6-inch pipe the cost is increased only 16% from $4.86 to $5.62 per ft. Similarly, a 2.86-fold increase in capacity is obtained in a change form 16-inch to 24-inch Lock Joint pipe for an increase in cost of only 58%.

The 1954 A.W.W.A. Committee states that an accurate deter-

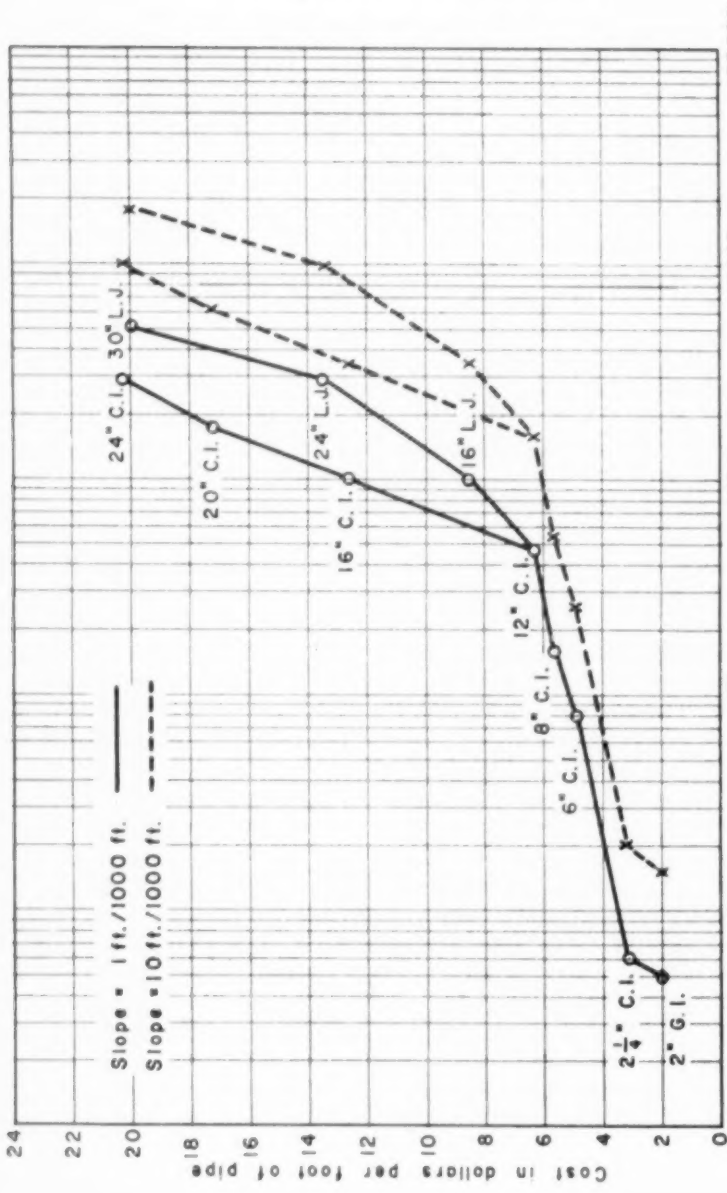

FIG. 1.—RELATION OF COST TO CAPACITY OF DISTRIBUTION MAINS.

mination of the incremental cost of a distribution system chargeable to fire protection would require cost estimates based on two systems, one for fire only and the second with capacity for both fire and general service. Before accurate cost estimates could be prepared, a preliminary design of at least one of the two systems would have to be prepared. The high cost of this procedure has prevented its adoption generally. In general, we agree with the soundness of this method, but we do not believe that accurate determinations of cost are possible by any method primarily because of the uncertainty as to the weight the courts will give to original cost and to reproduction cost. The method of computing fire-protection charges developed by our firm is an application of the A.W.W.A. method described above, modified to avoid the necessity of a preliminary design of a hypothetical system. Our method is illustrated hereinafter by a typical example.

An alternative approach is suggested by the 1954 A.W.W.A. Committee, to avoid the expensive procedure of making accurate cost estimates on two systems. This alternative approach involves the assumption that storage may be provided in lieu of capacity. This method is purely arbitrary and in our judgment has nothing to recommend it. The cost of hypothetical storage bears no relation to the additional cost of a distribution system required to furnish public fire protection. In its example to illustrate this alternative approach, the Committee adds to the cost of the hypothetical distribution storage the difference in cost of the distribution mains based upon a 4-inch differential in pipe size. It is difficult to understand this procedure. It would seem that either the cost of the hypothetical distribution storage or the cost of the additional main capacity might be used, but not both.

The adoption of a 4-inch differential in pipe size to estimate the additional cost of the distribution mains for fire protection is purely arbitrary. Our method of estimating the difference in the cost of the two systems is based upon a differential in pipe size computed rationally from the flow requirements. As will be shown later our figures indicate that a 4-inch differential is too great. Our studies show, moreover, that the differential should not be charged to large distribution arteries in large cities, because the capacity requirement for peak hourly flow will exceed the capacity requirement for fire flow plus maximum daily flow.

Determination of Public Fire-Protection Rates

Fundamental Principles Used in Determining Public Fire-Protection Rates

In our consideration of the cost of furnishing public fire protection for a city with a population of 12,000, supplied by a private water company, the first step was to select methods to use in allocating the cost between general consumption and fire protection. After study of the thinking and methods proposed by the various authorities who have considered this problem, it is our firm conviction that public fire protection as an incremental cost is the most equitable method.

In establishing rates to be charged by public utilities, the Smyth vs. Ames decision of the U.S. Supreme Court in 1898 is the basis of the law of the land. The legal principle set forth in this case is that the utility owners are entitled to a fair rate of return upon the present fair value of the property used and useful in rendering the public service. In determining fair values this decision maintained that all factors affecting fair values must be given the weight due in each case. The following is quoted from this decision: "In order to ascertain the fair value, original cost of construction, amount expended in permanent improvements, the amount and market value of its bonds and stocks, the present as compared with the original cost of construction, the probable earning capacity of the property under particular rates prescribed by statute, and the sum required to meet operating expenses, are all matters for consideration and are to be given such weight as may be just and right in each case. We do not say that there may not be other matters to be regarded in estimating the value of the property. But the company is entitled to ask a fair return upon the value of that which it employs for the public convenience. On the other hand, what the public is entitled to demand is that no more be exacted from it for the use of a public facility than the services rendered by it are reasonably worth."

The two limiting methods for determining fair value of property involved are: (1) the actual legitimate cost of the utility's property less depreciation and (2) the present-day reproduction cost less the depreciation values based on the reproduction cost. There has been much controversy concerning what relative weight should be given

to each of the above limits in arriving at fair value of property under consideration. We have used both of these limiting conditions to estimate the cost of fire protection in the example which follows. The rate for fire protection established under these assumption is for public fire protection. The cost thereof is directly assignable to the taxpayers of the City served by the Water Company, and is most feasibly charged directly to the City and paid for by the City and the cost thereof distributed to the taxpayers of the City by the normal taxing procedures.

Computations for Determining Rates for Public Fire Protection by the Incremental Method

In this study the basic data used for making the computations were obtained from the records of the Water Company.

The water consumption data were taken from the Company's daily meter readings. The maximum daily consumption during the past three years was as follows:

July 10, 1952	1,470,000 gal.
July 8, 1951	1,400,000 gal.
July 11, 1950	1,446,000 gal.

For this study a maximum daily consumption of 1.5 mgd was used. No records were available of the peak consumption and this was estimated at 3 mgd or approximately twice the average on the maximum day.

In plotting the curves shown on Fig. 2 for maximum daily and peak domestic flows, the ratio on the maximum day of the peak flow to the average flow was assumed to vary from about three for the smaller populations to about two for the larger populations. In estimating the maximum fire flows, we have used the requirements of the National Board of Fire Underwriters, as represented by the formula $Q = \sqrt{x}\ (1\text{-}0.01\ \sqrt{x})$, where Q is in gpm and x is the population in thousands. In case the fire requirements, as established in conformity with the National Board of Fire Underwriters' Bulletin No. 266, are different from those given by the formula, the actual requirements should be correlated with the population of the city and portions thereof, and used instead of the requirements given by the formula.

In this study we have assumed that the capacity of the existing

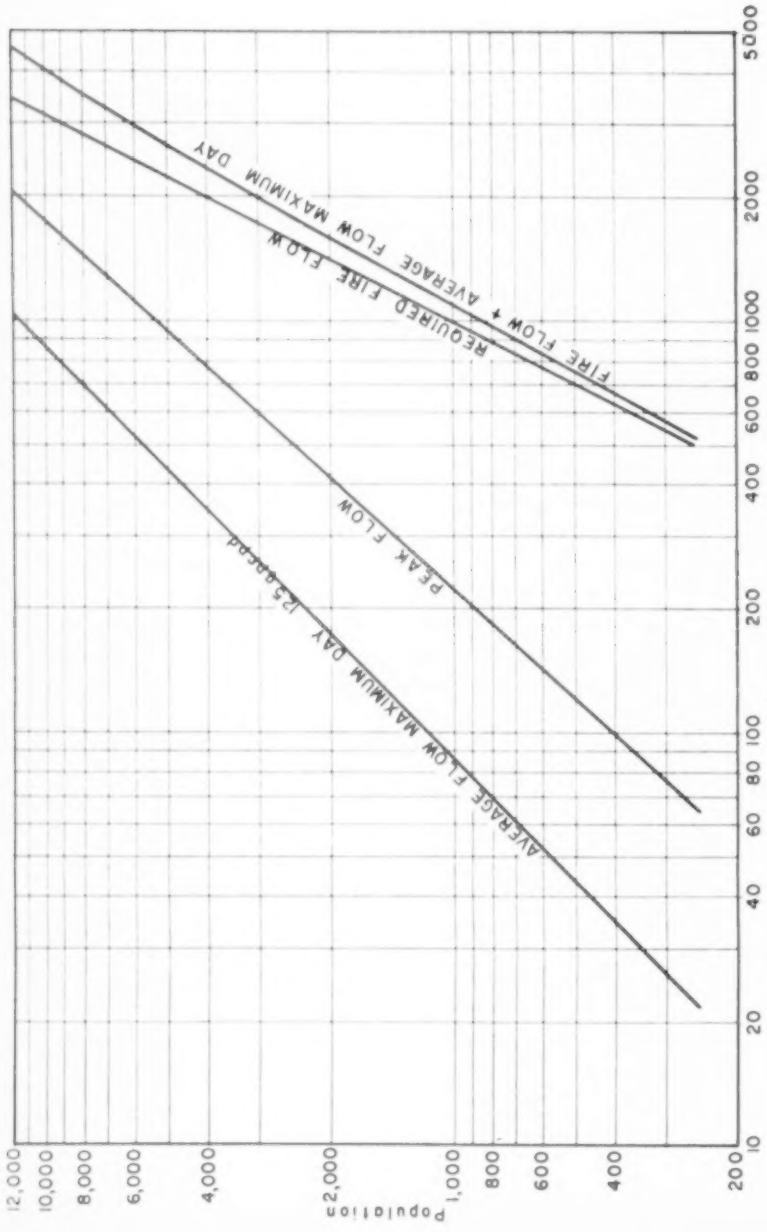

FIG. 2.—ESTIMATED PRESENT FLOWS FOR CITY IN TERMS OF POPULATION SERVED.

distribution system is equal to the requirements of the National Board of Fire Underwriters, that is, that fire flows represented by the formula are available concurrently with a general demand equal to the maximum daily consumption. If the existing distribution system does not meet these requirements, it is not necessary to adjust the computations to reflect the deficiencies of the system. Since the result sought is the incremental cost of fire protection and this increment is obtained by deductions from the existing system, the increment will not be substantially changed by adjustments to reflect the inadequacies of the existing system.

In determining the per cent of the total value of the distribution system chargeable to fire flow, it is necessary to compare the cost of the existing system with the cost of a hypothetical system having no fire-flow capacity. The standards of the N.B.F.U., which in our opinion are reasonable, require that the system be capable of delivering an adequate fire flow simultaneously with a normal draft equal to the maximum daily demand. We see no reason for assuming that the maximum fire flows will occur simultaneously with peak demand, as has been assumed in some studies of this problem. Regardless of whether or not fire-flow capacity is provided, a well designed waterworks system must be capable of delivering a flow equal to the peak draft or peak hourly demand to be expected during the year.

In comparing the existing distribution system of pipes 6-in. and larger (pipes smaller than 6-in. are not adequate for fire protection and were assigned only to the distribution of domestic supply) against a hypothetical system for general service only, we have assumed that the latter system requires capacities adequate to supply peak demands. In other words, we believe that the capacity in the system chargeable to fire protection is equal to the maximum daily demand plus the maximum fire flows minus the peak demands. For example, for a population of 250, the fire flow plus the maximum daily flow, from Fig. 2, is 520 gpm and the peak flow is 65 gpm. The difference of 455 gpm, or 87.5% of the total, is chargeable to public fire protection. Similarly, for a population of 12,000, the fire flow plus maximum daily demand is 4,500 gpm and the peak flow is 2,080 gpm. The difference of 2,420, or 53.8% of the total, is chargeable to public fire protection. These additional capacities, large as they are, are to be charged for on

the basis of the additional cost of the pipes now in the system.

The sizes of pipes in the distribution system for the hypothetical case of supplying domestic consumption only were obtained by using the Hazen & Williams expression for flow in pipes. With any given hydraulic gradient and friction factor, the flow is proportional to the 2.63-power of the diameter, thus

$$Q_2 = Q_1 \left(\frac{D_2}{D_1}\right)^{2.63}$$

From this a hypothetical pipe of diameter D_2 can be determined which will give a flow capacity, Q_2, equal to a given per cent of the flow capacity, Q_1, in a corresponding pipe of diameter D_1 in the actual system. The values of Q_2 and Q_1 for any population within the system may be taken from Fig. 1, where Q_2 is the peak flow and Q_1 is the maximum daily flow plus the fire flow. If it is assumed that any given pipe, 6 in. in diameter or larger, in the distribution system is adequate for providing fire flows plus maximum demand, then from Fig. 2 and the above formula the diameter of the corresponding pipe in the hypothetical system may be computed.

The results of computations as described above are presented in Table 1 for populations from 250 to 12,000. The ratios $\frac{Q_2}{Q_1}$ of peak demand to the sum of maximum daily and fire demand, as shown in the second column, were determined from Fig. 2. The headings of the last four columns show the pipe sizes in the existing system. Under each size of existing pipe and opposite a given population are two columns. The first column shows the theoretical pipe sizes required to supply peak flows only, as computed from the equation. The second column shows the nearest standard pipe size sufficient to provide the peak flow only. This is a reasonable consideration, since in the final cost analysis it is reasonable to use only available pipe sizes. The pipe sizes for the hypothetical system have been computed only for populations which may reasonably be served by existing sizes at the head of each column. These limitations were determined by a study of the distribution system in question.

It will be noted from Table 1 that most of the existing 6-inch pipe would be replaced by 3-inch to produce the hypothetical system;

TABLE 1.—SIZES REQUIRED FOR A HYPOTHETICAL SYSTEM SUPPLYING DOMESTIC CONSUMPTION ONLY

Population	$\left(\frac{\frac{Q_2}{Q_1}}{\frac{peak}{fire + max.\ day}}\right)$	$\left(\frac{Q_2}{Q_1}\right)\frac{1}{2.63}$	Sizes in present system							
			6"		8"		10"		12"	
			Req.	Use	Req.	Use	Req.	Use	Req.	Use
250	0.128	0.458	2.74	3						
500	0.161	0.500	3.00	3						
750	0.186	0.528	3.17	3	4.23	4				
1,000	0.208	0.551	3.31	4	4.40	6	5.51	6		
2,000	0.263	0.602			4.81	6	6.02	6	7.22	8
5,000	0.358	0.676					6.76	8	8.11	8
8,000	0.414	0.715							8.58	10
10,000	0.436	0.729								
12,000	0.470	0.750								
			Use	3"	Use	6"	Use	6"	Use	8"

most of the 8-inch by 6-inch; most of the 10-inch by 6-inch and most of the 12-inch by 8-inch. In our computations to determine the cost of the hypothetical system, we have used the above replacement sizes. The sizes used are indicated at the bottom of Table 1.

Table 2 gives the length, sizes and original costs of the distribution mains as of December 31, 1952. These figures are available in the records of most private water utilities and should be available for a publicly-owned water works.

TABLE 2.—COSTS OF DISTRIBUTION SYSTEM AS OF DECEMBER 31, 1952
INITIAL COSTS

Size	*Units*	*Unit cost*	*Total*
Cement-Lined Pipe			
12″	2,682′	$ 1.30	$ 3,486.60
10″	2,271′	1.00	2,271.00
8″	4,019′	0.85	3,416.15
6″	27,272′	0.72	19,635.84
4″	446′	0.65	289.90
Cast-Iron Pipe			
12″	30,339′	6.99	211,999.35
10″	7,763′	4.91	38,116.61
8″	8,903′	3.95	35,139.07
6″	62,216′	2.33	144,664.01
4″	5,137′	1.16	5,939.59
Wrought-Iron Pipe			
2″	44,413′	1.89	83,968.59
1½″	18,315′	0.72	13,160.38
1¼″	5,513′	1.03	5,662.71
1″	1,621′	0.94	1,519.31
Gates			
12″	67	112.33	7,525.90
10″	13	78.00	1,014.02
8″	23	68.11	1,566.57
6″	180	46.47	8,365.10
4″	10	20.56	205.55
2″	102	19.15	1,953.46
1½″	42	12.04	505.72
1¼″	16	13.27	212.24
1″	11	6.71	73.76
Total December 31, 1952 —			$590,691.43

The estimated difference in cost between a hypothetical system which is capable of delivering the peak demand on the maximum day for domestic consumption only and the actual system is given in Table 3. The sizes were obtained from Table 1 and the costs for those sizes were obtained from Table 2. Table 3 shows an incremental cost of the distribution system for fire protection of $211,866, based on original cost, which is equivalent to 35.87% of the total cost of the distribution system. This figure has been used to allocate the distribution-system value, as shown in Table 4.

TABLE 3.—INCREMENTAL COST OF DISTRIBUTION SYSTEM FOR FIRE PROTECTION BASED ON TABLES 1 AND 2

		Present system		*Domestic only*	
Size	*Price*	*Length*	*Cost*	*Length*	*Cost*
Cement Pipe					
12″	$1.30 per ft	2,682 ft	$ 3,487		
10″	1.00	2,271	2,271		
8″	0.85	4,019	3,416	2,682 ft	$ 2,280
6″	0.72	27,272	19,636	6,290	4,529
4″	0.65				
3″	0.65*			27,272	17,727
Cast-Iron					
12″	6.99 per ft	30,339 ft	211,999		
10″	4.91	7,763	38,117		
8″	3.95	8,903	35,139	30,339 ft	119,839
6″	2.33	62,216	144,644	16,666	38,832
4″	1.16				
3″	1.16*			62,216	72,171
Gates		*Number*		*Number*	
12″	112.33 each	67	7,526		
10″	78.00	13	1,014		
8″	68.11	23	1,567	67	4,563
6″	46.47	180	8,365	36	1,673
4″	20.56				
3″	20.56*			180	3,701
			$477,181		$265,315
			265,315		
Incremental Cost for Fire Protection			$211,866		

*Prices for 3″ hypothetical sizes assumed to be the same as the prices for existing 4″ sizes.

TABLE 4.—ALLOCATION OF FIXED ASSETS INITIAL COSTS

	Total account	*Sub-divisions*	*General Service*		*Fire*		*Undistributed*	
			%	*$*	*%*	*$*	*%*	*$*
LAND	$ 6,983							
Power and Pumping		$ 3,025	100.00	$ 3,025				
Reservoir and Tank		3,958	79.38	3,142	20.62	$ 816		
STRUCTURES	114,643							
Source of Supply		2,112	100.00	2,112				
Pumping Station:								
Pump Room		6,175	100.00	6,175				
Meter Room		5,575	100.00	5,575				
Heating System		1,499					100.00	$ 1,499
Reservoir		11,339	100.00	11,339				
Tank		65,891			100.00	65,891		
General and Misc. Buildings		22,052					100.00	22,052
PRODUCTION EQUIP-MENT	14,037							
Electric Pump		9,483	100.00	9,483				
Standby Pump		2,814			100.00	2,814		
Purification Equiment		1,740	100.00	1,740				

TABLE 4 *(continued)*

TRANSMISSION and DISTRIBUTION	799,675							
Transmission Mains		14,618	100.00	14,618				
Transmission to New Tank		3,846			100.00	3,846		
Distribution System		590,691	64.13	378,825	35.87	211,866		
Services		105,365	100.00	105,365				
Meters		54,575	100.00	54,575				
Hydrants		27,132			100.00	27,132		
Sprinkler Services (Private Fire Protection Only)		3,448						
GENERAL EQUIPMENT	21,633						100.00	21,633
MISCELLANEOUS PROPERTY	12,281						100.00	12,681
Total of Fixed Assets	$969,252							
Less Sprinkler Services	3,448							
Total Assets to be Distributed	$965,804			$595,974		$312,365		$57,465
Distribution of Undistributed				37,703		19,762		
				$633,677		$332,127		
Distribution of Costs			65.61%		34.39%			

The fixed assets of the water works were taken from figures prepared by the management. These figures are shown in Table 4. The allocation of these fixed assets is based upon the principle of incremental charges for fire service, in conformance with which such items as pumping station, the electric pumps, transmission main and reservoir were determined to be required by a system which would supply domestic consumption only under methods of operation now employed by the water works. For example, one electric pump operating for approximately 10 hours will produce 1.5 mgd or approximately the maximum demand of the present consumers. Since pumping is done only during off-peak hours and is limited to approximately 10 hours, it was deemed necessary that a pump of this size would be required for domestic service only. The second pump would also be required for standby purposes. The 14-inch transmission main was found necessary to deliver this quantity of water to the reservoir. The items applicable to fire protection only are hydrants, fire-service connections, the new elevated tank and the transmission main to the elevated tank, land for the elevated tank and the fire-protection share of the undistributed items.

The fixed assets listed in Table 4 are allocated to three different classifications; namely, General Service, Fire and Undistributed. The assets allocated to Fire are those items used only in fire protection and are the new elevated tank, hydrants, and similar items. Certain items of fixed assets are not easily assignable to any classifications and are allocated to Undistributed. Such items are used in part by the other two classifications and consist of general equipment, miscellaneous property, buildings, etc.

After the assets are assigned to these various classifications, they are totalled and the undistributed total is distributed between General Service and Fire in direct ratio of the total of each of these items to the total of these two items. After this distribution of the undistributed amounts, the percentage of the fixed assets under each heading is figured, and the percentages are listed at the bottom of Table 4. The final percentage of the fixed assets which is allocable to fire protection is 34.39%.

The amount of revenue which is derived from the fixed assets of the water works is assigned to fire protection in the percentage of

34.39 as determined above. To this figure must be added the amount of operation and maintenance expense which is assignable to fire protection and consists of such items as maintenance of hydrants and the fire-protection portion of the undistributed overhead expense. In this particular case the amount of operation and maintenance expense chargeable to fire protection was determined to be 7.70%. The total revenue chargeable to fire protection was then determined to be 24.42% of the total revenues of the water company.

The figure of 24.42% given above was based upon the book cost or actual out-of-pocket original cost. A similar computation was made on the basis of present-day reproduction cost and a figure of 17.70% of the revenues, based on reproduction-cost method, was arrived at. The actual fire-protection charges in these cases were $34,500 for the case based on book cost and $35,800 for the case based on reproduction cost. We recommended, therefore, a value of $35,000 as being the fair charge for fire-protection service. It will be noted that for this case the fire-protection charge was practically the same with book value and reproduction value. In most cases a wide divergence may be expected.

Computations for Determining Rates for Public Fire Protection by the Metcalf, Kuichling and Hawley Formula

Let us now consider the fire-protection charges based on some other methods for figuring the charge. If we use the Metcalf, Kuichling and Hawley equation for a population of 12,000, the percentage of the total cost of the water works involved in fire protection is 56%. The 56% ratio corresponds with the 34.39% derived by our method. After the fire-protection portion of the operation and maintenance cost has been added, the total percentage of revenue chargeable to fire protection is 36.2%. This is in contrast to the 24.4% arrived at by our method.

Computations for Determining Rates for Public Fire Protection by the Capacity-Ratio Method

The capacity-ratio method, as recommended by the Joint Committee of the American Society of Civil Engineers and the Section of Municipal Law of the American Bar Association, involves two proce-

dures for figuring the ratio, one based on the costs of the systems and the other on the capacities.

In both procedures, two systems are considered, one to provide public fire protection only and one to provide general service only. In the first procedure, the jointly used facilities in the actual system are then allocated between fire protection and other uses on the ratio of fire-protection-plant cost to the sum of fire-protection-plant cost and general-service-plant cost. The other procedure is to make the allocation on the basis of the demand for water, and the ratio in this case has in its numerator the maximum demand for fire protection and in its denominator the demand for fire protection plus the maximum general-service demand.

By using the costs of the distribution system which have been developed for the incremental-cost method, it was possible to arrive at the cost of the distribution system for fire protection only, and the cost of a distribution system for fire protection only plus the cost of the distribution system for domestic service only. When this fraction was applied to the revenue to be derived from the fixed assets and the operation and maintenance expenses had been taken into account, it was determined that 35.9% of the revenues for the water works should be derived from fire-protection service. The same figure, using the demands of the fire-protection system and the demands of the domestic system for determining the fraction, produced a percentage of the gross revenue of 35.5% to be derived from fire protection. These figures are again contrasted to the 24.4% obtained by our method.

Actual Charges

A study of the "Survey of Operating Data for Water Works in 1950", a staff report published in the June, 1953, *Journal of the American Water Works Association*, indicated that for 46 private water companies only one company had a percentage of total revenue derived from fire protection greater than 20%, only seven had a percentage greater than 10%, and five derived no revenue for fire-protection service. A similar analysis of the revenue from municipally-owned water works would undoubtedly indicate that a much smaller percentage of revenue is derived from fire-protection service than is indicated for private water companies.

Conclusions

(1) It is erroneous to assume that the cost of the distribution system, which represents the greater part of the cost of most water systems, is proportional to the capacity of the system. This erroneous assumption was first made by Metcalf, Kuichling and Hawley in 1911 and is still used by current writers on this subject.

(2) If this assumption is used in computing the fire-protection charges by all three of the general methods defined by the Joint Committee and the same flows are used in the computations, indentical results will be obtained for that portion of the undivided fixed assets of the water works chargeable to fire protection.

(3) The alternative approach suggested by the 1954 AWWA Committee is in error because it assigns a storage charge in lieu of capacity and also a differential pipe charge to fire protection. If a storage charge is used in lieu of capacity, then we believe it is in error to charge also for the additional main capacity. Our studies show that the 4-in. pipe size differential used by the committee is too large.

(4) We have developed and presented herein a method of computing fire-protection charges which we believe to be equitable and free from basic error. It is based on the philosophy that the cost of fire protection should be considered as an incremental cost over and above the cost of general service. The cost of fire protection obtained by our method is substantially less than the cost computed by all other methods commonly used.

(5) The actual charge for fire-protection services made by both private water companies and municipally-owned water works is in most cases substantially below what the taxpayer should pay for the benefits he is receiving. The general rate payer is therefore paying more for the water he uses than is his equitable share. We hope that our method will be utilized to fix charges for fire-protection services commensurate with the service received, and that the general rate payer will thereby be relieved of the unjust burden he is now carrying.

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PROCEEDINGS

November 1954 Meeting

Hotel Statler, Boston, Mass.

Thursday, November 18, 1954

President Roger G. Oakman in the Chair.

Secretary Knox announced the election of the following to membership in the Association:

Charles H. Campbell, Superintendent, Water Dept., Littleton, Mass.; John V. Richards, Sanitary Engineer, State Dept. Health, Burlington, Vt.; Edward Endelson, Treasurer, Bondsville Water Co., Bondsville, Mass.; Richard G. Small, Assistant Treasurer, Portland Water District, Portland, Me.

Associate Member:

Aetna Enginering Co., Ashaway, R. I.

Papers on "Experiences During the Recent Hurricanes," illustrated by stereopticon slides, were read as follows:

Fred P. Stradling, Manager, Bristol County Water Co., Bristol, R. I.

Paul T. Anderson, District Engineer, Massachusetts Department of Public Health, Middleborough, Mass.

Thomas J. Rinaldo, Sanitary Engineer, Metropolitan District Commission, Water Division, Framingham, Mass.

DECEMBER 1954 MEETING

HOTEL STATLER, BOSTON, MASS.

THURSDAY, DECEMBER 16, 1954.

President Roger G. Oakman in the Chair.

Secretary Knox announced the election of the following to membership in the Association:

Kenneth G. Barnhill, Sales Engineer, The Permutit Co., Boston, Mass.; Dale E. Caruthers, Portland Water District, Portland, Me.; Tsuan Hua Feng, Assistant Professor of Sanitary Engineering, University of Massachusetts, Amherst, Mass.; Lorrin S. Brice, Builders Iron Foundry, Providence, R. I.; Donald R. Harleman, Assistant Professor of Hydraulics, Massachusetts Institute of Technology, Cambridge, Mass.

There followed considerable discussion on the question of establishment of an annual freshman scholarship, not to exceed $500, at the Massachusetts Institute of Technology for the sons and daughters of members of this Association. Upon motion duly made and seconded, it was VOTED that the scholarship-fund matter be laid on the table.

Then, upon motion of E. Sherman Chase, duly seconded, it was VOTED that the President be authorized to appoint a committee, not exceeding five, to study methods for putting an Association-sponsored scholarship into operation, said committee to submit a report to the Association prior to the next annual meeting, for action at that time upon such recommendations as said report may contain.

A paper on "New England in Focus" was read by Richard E. Fiske, News Director, The New England Council, Boston, Mass.

A paper on "A Report on Improvements to the New Bedford Water System" was read by Howard C. Mandell, Superintendent of Water Works, New Bedford, Mass.

A film, "Potable Water in Puerto Rico," produced by Puerto Rico Aqueduct and Sewer Authority, was shown through the courtesy of Buck, Seifert & Jost, New York, N. Y.

JANUARY 1955 MEETING

HOTEL STATLER, BOSTON, MASS.

THURSDAY, JANUARY 20, 1955.

President Roger G. Oakman in the Chair.

Secretary Knox announced the election of the following to membership in the Association:

John F. Collins, Superintendent and Engineer, Water Works, Greenfield, Mass.; Howard W. Ford, Retired, formerly Vice-President and Director, Pittsburgh-Des Moines Steel Co., Madison, N. J.; George K. Pierce, Superintendent, Barnstable Water Co., Hyannis, Mass.; Kenneth H. Walker, Sales Engineer, Wallace & Tiernan Co., Inc., Waban, Mass.; O. Milton Hackett, Geologist-in-charge, Ground Water Branch, U.S. Geological Survey, Boston, Mass.; John S. Lovewell, with Metcalf & Eddy, Boston, Mass.

Associate Member:

Graver Water Conditioning Co., New York, N. Y.

President Oakman announced the appointment of the following to the Scholarship Committee:

William B. Duffy, Chairman, Thomas R. Camp, Roger W. Esty, Kenneth F. Knowlton and Thomas S. Lawrence.

A paper on "New and Interesting Features in Relation to Gravel-Packed Wells and Pumping Plants at Provincetown and Centerville-Osterville, Mass." was read by Paul F. Howard, Whitman & Howard, Consulting Engineers, Boston, Mass.

A paper on "New Asphalt-Lined Reservoir for Rutland, Vermont" was read by Edward L. Tracy, Director, Division of Sanitary Engineering, State Department of Health, Burlington, Vt.

INDEX OF ADVERTISERS

	Page
Anderson-Nichols & Co.	iii
Badger Meter Mfg. Co.	Following front cover
Bahr, Ray	xx
B-I-F Industries, Inc.	Following front cover
Brown Co.	xx
Calgon, Inc.	Following front cover
Camp, Dresser & McKee	ii
Cast Iron Pipe Research Assn.	xxvii
Cement Lined Pipe Co.	xx
Centriline Corp.	Following front cover
Chapman Co., R. E.	ii
Chicago Bridge & Iron Co.	xxi
Coffin and Richardson	ii
Crosby, Irving B.	ii
Eddy Valve Co.	xiv
Eureka Pipe Co., Inc.	xvi
Fairbanks, Morse & Co.	Following front cover
Fay, Spofford & Thorndike	ii
Flexible Sales Corporation	xx
Ford Meter Box Co.	Following front cover
Gunite Restoration Co., Inc.	ii
Haley & Ward	ii
Hays Mfg. Co.	xv
Hazen & Sawyer	iii
Hersey Mfg. Co.	iv
Hilco Supply	xxi
Hydraulic Development Corp.	ix
Johns Manville Sales Corp.	x
Keasbey & Mattison Co.	vii
Kennedy Valve Mfg. Co.	xvii
Knowles, Inc., Morris	ii
Layne-New York Co.	iii
Leadite Co.	Back cover
Leggette & Brashears	ii
Lock Joint Pipe Co.	Following front cover
Maguire & Assoc., Chas. A.	iii
Maher Co., D. L.	iii
Metcalf & Eddy	ii
Mills Engineering Co., Inc.	xvi
Morris Knowles, Inc.	ii
Mueller Co.	Following front cover
National Water Main Cleaning Co.	xii
Neptune Meter Co.	xi
Pierce-Perry Co.	iii
Pipe Founders Sales Corp.	xvi
Pirnie, Malcolm	iii
Pitometer Assoc., Inc., The	iii
Pittsburgh-Des Moines Steel Co.	Following front cover
Pittsburgh Equitable Meter Div.	Following front cover
Pollard Co., Inc., Joseph G.	Following front cover
Pratt Co., Henry	vi
Prescott & Sons, Inc., H. R.	xviii
Public Works Supply Co.	xx
Rensselaer Valve Co.	v
Ross Valve Mfg. Co.	xix
Smith Mfg. Co., The A. P.	Following front cover
Turbine Equipment Co. of New England	Following front cover
U. S. Cast Iron Pipe & Foundry Co.	xxviii
Wallace & Tiernan Co., Inc.	xiii
Warren Foundry & Pipe Corp.	Following front cover
Weston & Sampson	iii
White Construction Co., R. H.	xvi
Whitman & Howard	iii
Wood Co., R. D.	Following front cover
Worthington-Gamon Meter Div.	viii

(Classified index on page xxiii)

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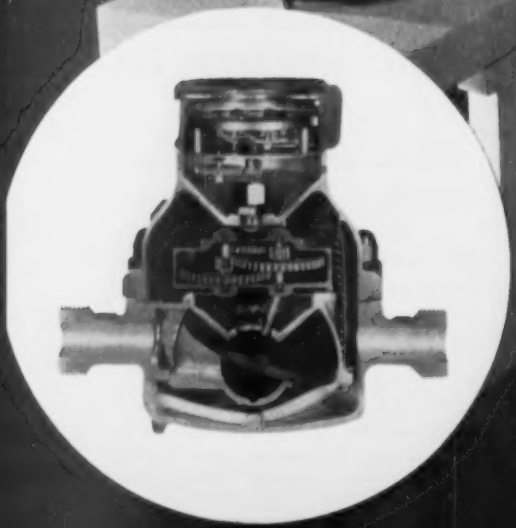

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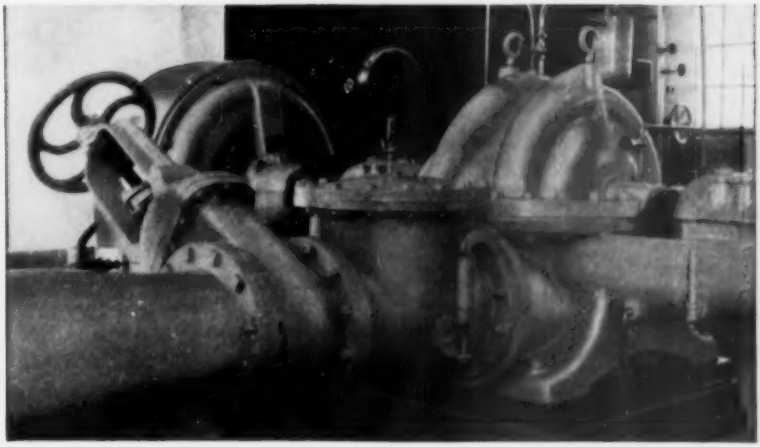

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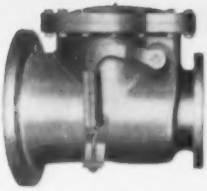

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Heavy slams can cause damages of explosive proportions. Modest slams may throw piping out of alignment and cause serious leakages.

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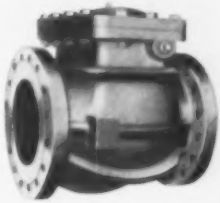

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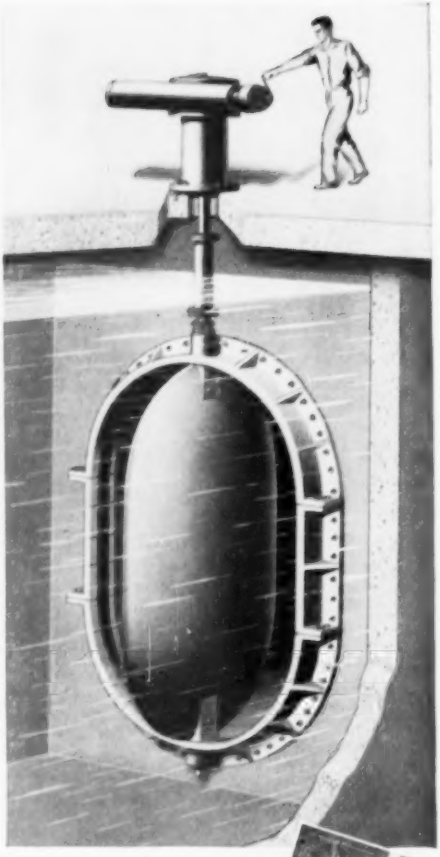

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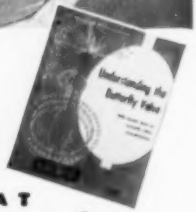

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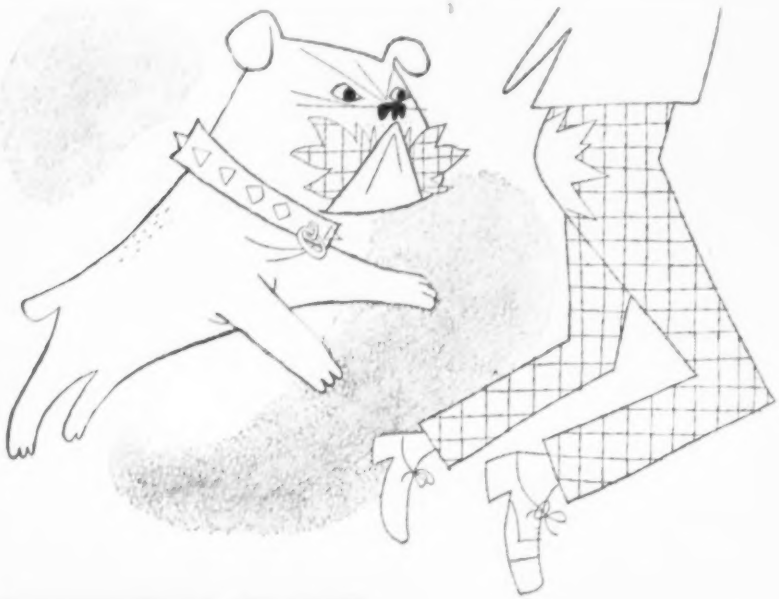

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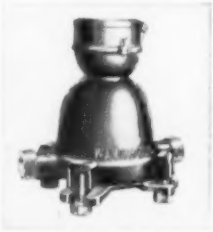

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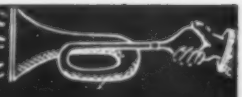

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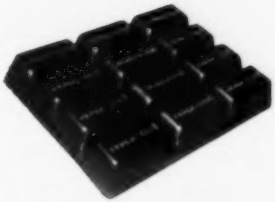

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here's what "out of sight out of mind" does to a water main

"Out of sight—out of mind" can be a mighty expensive philosophy in any water distribution system. The above unretouched photograph proves this point. It shows a badly tuberculated *eight inch* main whose *inside diameter was reduced to an average of almost 4.5 inches.* Resultant higher pumping costs with reduced pressure and carrying capacity make it costly to tolerate such conditions. That is why the savings effected in reduced pumping costs frequently pay for the *low cost* of National water main cleaning.

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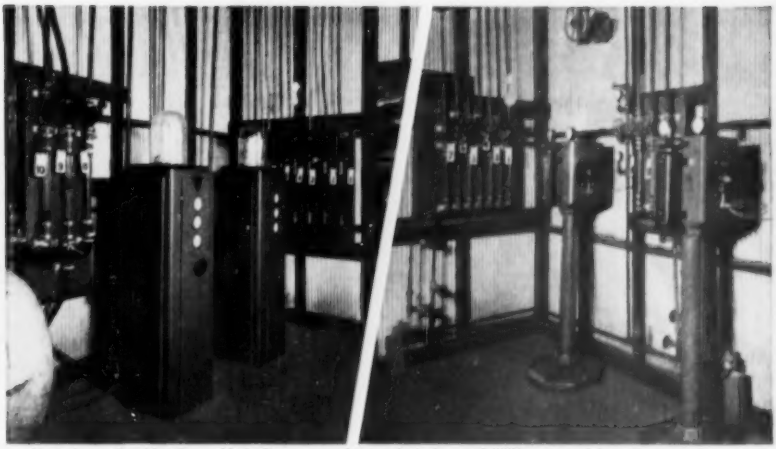

Two views of midwestern chlorinating room showing typical use of W&T equipment to suit a specific need.

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How well chlorination equipment does its job depends not only on proper design but on the selection of the right parts and materials for every specific purpose.

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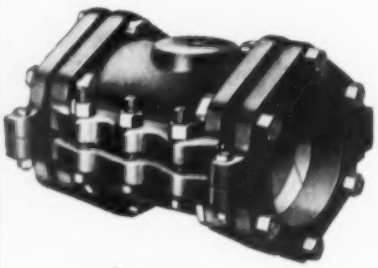

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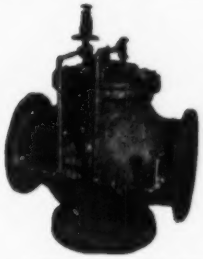

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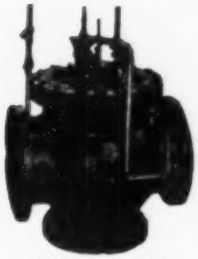

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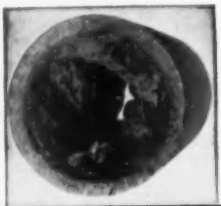

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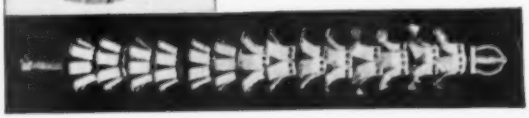

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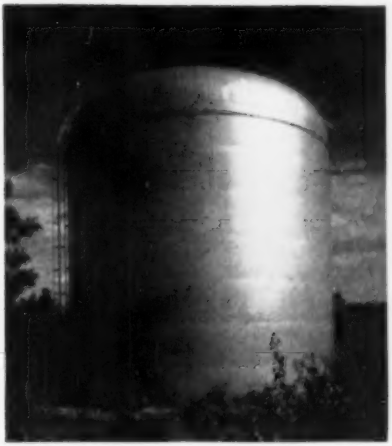

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CLASSIFIED DIRECTORY OF ADVERTISEMENTS

ASBESTOS-CEMENT PIPE.
Keasbey & Mattison Company vii

BRASS GOODS.
Eureka Cement Lined Pipe Co. xvi
Hays Mfg. Co. xv
Hilco Supply xvi
Mueller Co. ..... Following front cover
Pierce-Perry Co. iii

CALKING MACHINERY AND TOOLS.
Hydraulic Development Corp. ix
Mueller Co. ..... Following front cover

CAST IRON PIPE. (See Pipe, Cast Iron.)

CEMENT LINED PIPE. (See Pipe, Cement Lined.)

CHEMICAL FEED APPARATUS.
B-I-F Industries ..... Following front cover
℄ Proportioneers, Inc. ℄ (B-I-F Industries, Inc.) ..... Following front cover
Wallace & Tiernan Co., Inc. xiii

CHLORINATORS.
B-I-F Industries ..... Following front cover
℄ Proportioneers, Inc. ℄ (B-I-F Industries, Inc.) ..... Following front cover
Wallace & Tiernan Co., Inc. xiii

CLARIFIERS.
Mills Engineering Co., Inc. xvi

CLEANING WATER MAINS.
Flexible Pipe Cleaning Co. xx
National Water Main Cleaning Co. xii

COCKS, CURBS AND CORPORATIONS.
Eureka Cement Lined Pipe Co. xvi
Hays Mfg. Co. xv
Mueller Co. ..... Following front cover
Pierce-Perry Co. iii

CONCRETE PIPE. (See Pipe, Concrete.)

CONTRACTORS' EQUIPMENT.
Hydraulic Development Corp. ix

CONTRACTORS.
Layne-New York Co., Inc. iii
Maher, D. L. Co. iii
White Construction Co., R. H. xvi

CORROSION CONTROL.
Calgon, Inc. ..... Following front cover

COUPLINGS, FLEXIBLE PIPE.
Public Works Supply Company xx

CURB BOXES.
Eureka Cement Lined Pipe Co. xvi
Hays Mfg. Co. xv
Hilco Supply xvi
Mueller Co. ..... Following front cover
Pierce-Perry Co. iii
H. R. Prescott & Sons, Inc. xviii
Public Works Supply Company xx

DIAPHRAGMS, PUMPS.
Joseph G. Pollard Co. ..... Following front cover
℄ Proportioneers, Inc. ℄ (B-I-F Industries, Inc.) ..... Following front cover

EJECTOR, PNEUMATIC.
Mills Engineering Co., Inc. xvi

ENGINEERS.
Anderson-Nichols & Co. iii
Camp, Dresser & McKee ii
Coffin & Richardson ii
Crosby, Irving B. ii
Fay, Spofford and Thorndike ii
Haley and Ward ii
Hazen and Sawyer iii
Knowles Morris, Inc. ii
Leggette & Brashears ii
Maguire & Associates, Charles A. iii
Metcalf and Eddy ii
Pirnie Engineers, Malcolm iii
Pitometer Associates, Inc., The iii
Weston and Sampson iii
Whitman and Howard iii

ENGINES. (See Pumps and Pumping Engines.)

EQUIPMENT. (See Contractors' Equipment.)

CLASSIFIED DIRECTORY OF ADVERTISEMENTS *(Continued)*

FEED WATER FILTERS.
% Proportioneers, Inc. % (B-I-F Industries, Inc.) ..... Following front cover
Ross Valve Mfg. Co., Inc. xix
FILTRATION PLANT EQUIPMENT.
B-I-F Industries ..... Following front cover
Mills Engineering Co., Inc. xvi
% Proportioneers, Inc. % (B-I-F Industries, Inc.) ..... Following front cover
FLAP VALVES.
Eddy Valve Co. xiv
FLEXIBLE JOINTS.
U. S. Pipe and Foundry Co. xxviii
FURNACES.
Hilco Supply xxi
Hydraulic Development Corp. ix
Leadite Co., The ..... Back cover
Mueller Co. ..... Following front cover
Pollard Co., Joseph G. ..... Following front cover
H. R. Prescott & Sons, Inc. xviii
Public Works Supply Company xx
GAS HOLDERS.
Chicago Bridge and Iron Co. xxi
GATE VALVES. (See Valves.)
GEARS.
Mills Engineering Co., Inc. xvi
GUNITE CONSTRUCTION.
Gunite-Restoration Co., Inc. ii
HOSE, SUCTION AND CONDUCTION.
H. R. Prescott & Sons, Inc. xviii
HYDRANTS, FIRE.
Eddy Valve Co. xiv
Hilco Supply xxi
Kennedy Valve Mfg. Co. xvii
Mueller Co. ..... Following front cover
H. R. Prescott & Sons, Inc. xviii
Public Works Supply Company xx
Rensselaer Valve Co. v
Smith Mfg. Co., The A. P. ..... Following front cover
Wood, R. D., Co. ..... Following front cover
HYDRANTS, PUMPS.
Hilco Supply xxi
Joseph G. Pollard Co. ..... Following front cover
H. R. Prescott & Sons, Inc. xviii
LEAD PIPE. (See Pipe, Lead.)
LIQUID CHLORINE.
Brown Co. xx
METERS, OIL AND WATER.
Badger Meter Mfg. Co. ..... Following front cover
B-I-F Industries ..... Following front cover
Hersey Mfg. Co. iv
Neptune Meter Co. xi
Pipe Founders Sales Corp. xvi
Pittsburgh Equitable Meter Div. ..... Following front cover
Worthington-Gamon Meter Div. viii
METER COUPLINGS.
Badger Meter Mfg. Co. ..... Following front cover
Ford Meter Box Co. ..... Following front cover
Hays Mfg. Co. xv
Hersey Mfg. Co. iv
Mueller Co. ..... Following front cover
Neptune Meter Co. xi
Public Works Supply Company xx
Worthington-Gamon Meter Div. viii
METERS (Venturi Type.)
B-I-F Industries ..... Following front cover
METER BOXES.
Ford Meter Box Co. ..... Following front cover
Mueller Co. ..... Following front cover
Public Works Supply Company xx
METER TESTERS.
Badger Meter Mfg. Co. ..... Following front cover
Ford Meter Box Co. ..... Following front cover
Mueller Co. ..... Following front cover
Neptune Meter Co. xi
Public Works Supply Company xx
OIL ENGINES.
Fairbanks, Morse & Co. ..... Following front cover
PIPE, ASBESTOS-CEMENT.
Keasbey & Mattison Company vii

CLASSIFIED DIRECTORY OF ADVERTISEMENTS *(Continued)*

PIPE, BRASS.
Hilco Supply ... xxi
Pierce-Perry Co. ... iii
H. R. Prescott & Sons, Inc. ... xviii

PIPE, CAST IRON (and Fittings.)
B-I-F Industries ... Following front cover
Cast Iron Pipe Research Association ... xxvii
Hilco Supply ... xxi
Pipe Founders Sales Corp. ... xxi
H. R. Prescott & Sons, Inc. ... xviii
U. S. Pipe and Foundry Co. ... xxviii
Warren Foundry and Pipe Co. ... Following front cover
Wood, R. D., Co. ... Following front cover

PIPE, CEMENT LINED.
Cast Iron Pipe Research Association ... xxvii
Cement Lined Pipe Co. ... xx
Eureka Cement Lined Pipe Co. ... xvi
Pipe Founders Sales Corp. ... xxi
U. S. Pipe and Foundry Co. ... xxviii

PIPE, COATING AND LININGS.
Centriline Corp. ... Following front cover

PIPE, CONCRETE.
Lock Joint Pipe Co. ... Facing front cover

PIPE CUTTING MACHINES.
Pollard Co., Joseph G. ... Following front cover
Smith Mfg. Co., The A. P. ... Following front cover

PIPE JOINTING MATERIAL.
Hilco Supply ... xxi
Hydraulic Development Corp. ... ix
Leadite Co., The ... Back cover

PIPE, LEAD.
Pierce-Perry Co. ... iii

PIPE LINING.
Cement Lined Pipe Co. ... xx
Centriline Corp. ... Following front cover

PIPE, PRESTRESSED CONCRETE.
Lock Joint Pipe Co. ... Facing front cover

PIPE, WROUGHT IRON AND STEEL.
Pierce-Perry Co. ... iii

PLUG VALVES.
Eddy Valve Co. ... xiv
Hays Mfg. Co. ... xv
Mueller Co. ... Following front cover
Pittsburgh Equitable Meter Div. ... Following front cover

PITOMETERS.
Pitometer Associates, Inc., The ... iii

PORTABLE AIR COMPRESSORS. (See Air Compressors.)

PRESSURE REGULATORS.
Hilco Supply ... xxi
Mueller Co. ... Following front cover
Pittsburgh Equitable Meter Div. ... Following front cover
H. R. Prescott & Sons, Inc. ... xviii
Ross Valve Mfg. Co., Inc. ... xiii

PROVERS, WATER.
Badger Meter Mfg. Co. ... Following front cover
Ford Meter Box Co. ... Following front cover

PUMPS AND PUMPING MACHINES.
Fairbanks, Morse & Co. ... Following front cover
Layne-New York Co., Inc. ... iii
Hilco Supply ... xxi
Maher Co., D. L. ... iii
Mills Engineering Co., Inc. ... xvi
Joseph G. Pollard Co. ... Following front cover
H. R. Prescott & Sons, Inc. ... xviii
Ross Valve Mfg. Co., Inc. ... xiii
Turbine Equipment Co. ... Following front cover
White Construction Co., R. H. ... xvi

RATE CONTROLLERS AND GAUGES.
Badger Meter Mfg. Co. ... Following front cover
B-I-F Industries ... Following front cover

REDUCERS, SPEED.
Mills Engineering Co., Inc. ... xvi

CLASSIFIED DIRECTORY OF ADVERTISEMENTS *(Continued)*

SHEAR GATES.
Eddy Valve Co. ... xiv
Mueller Co. ... Following front cover
SLEEVES AND VALVE TAPPINGS.
Eddy Valve Co. ... xiv
Hilco Supply ... xxi
Mueller Co. ... Following front cover
H. R. Prescott & Sons, Inc. ... xviii
Public Works Supply Company ... xx
Rensselaer Valve Co., Inc. ... v
Smith Mfg. Co., The A. P. ... Following front cover
SODIUM HEXAMETAPHOSPHATE.
Calgon, Inc. ... Following front cover
STAND PIPES.
Chicago Bridge and Iron Co. ... xxi
STEEL PLATE WORK.
Chicago Bridge and Iron Co. ... xxi
Pittsburgh-Des Moines Steel Co. ... Following front cover
STRAINERS.
Mills Engineering Co., Inc. ... xvi
SUPPLIES AND TOOLS.
Hilco Supply ... xxi
Hydraulic Development Corp. ... ix
Leadite Co., The ... Back cover
Mueller Co. ... Following front cover
Pierce-Perry Co. ... iii
Pollard Co., Joseph G. ... Following front cover
H. R. Prescott & Sons, Inc. ... xviii
Public Works Supply Company ... xx
TAPPING MACHINES.
Hays Mfg. Co. ... xv
Mueller Co. ... Following front cover
Smith Mfg. Co., The A. P. ... Following front cover
TANKS, STEEL.
Chicago Bridge and Iron Co. ... xxi
Pittsburgh-Des Moines Steel Co. ... Following front cover
TAPPING SLEEVES. (See Sleeves and Valves, Tappings.)
VALVE BOXES.
Eddy Valve Co. ... xiv
Hilco Supply ... xxi
Kennedy Valve Mfg. Co. ... xvii
Mueller Co. ... Following front cover
Pierce-Perry Co. ... iii
Pipe Founders Sales Corp. ... xviii
H. R. Prescott & Sons, Inc. ... xviii
Public Works Supply Company ... xx
Smith Mfg. Co., The A. P. ... Following front cover
Wood, R. D., Co. ... Following front cover
VALVES, BUTTERFLY.
Henry Pratt Co. ... vi
VALVE AND GATE GENERATORS.
Mills Engineering Co., Inc. ... xvi
VALVE INSERTING MACHINES.
Mueller Co. ... Following front cover
Smith Mfg. Co., The A. P. ... Following front cover
VALVES, CHLORINE.
Wallace & Tiernan Co., Inc. ... xiii
VALVES, GATE.
Eddy Valve Co. ... xiv
Hilco Supply ... xxi
Kennedy Valve Mfg. Co. ... xvii
Mueller Co. ... Following front cover
Pierce-Perry Co. ... iii
H. R. Prescott & Sons, Inc. ... xviii
Public Works Supply Company ... xx
Rensselaer Valve Co. ... v
Smith Mfg. Co., The A. P. ... Following front cover
Wood, R. D., Co. ... Following front cover
VALVES, REGULATING.
Mueller Co. ... Following front cover
Ross Valve Mfg. Co., Inc. ... xix
WASH FOUNTAINS.
Mills Engineering Co., Inc. ... xvi
WATER-PROOFING.
Gunite Restoration Co., Inc. ... ii
WATER WASTE DETECTION.
Pitometer Associates, Inc., The ... iii
WELLS, GRAVEL, FILTER AND DRIVEN.
Layne-New York Co., Inc. ... iii
Maher Co., D. L. ... iii
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